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PHYSICAL CHEMISTRY

For JEE (Main & Advanced)

Vipul Mehta

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For JEE (Main & Advanced)

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For JEE (Main & Advanced)

Adapted by
Vipul Mehta

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PHYSICAL CHEMISTRY
For JEE (Main & Advanced)

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Preface

Wiley Physical Chemistry for JEE (Main & Advanced) is a comprehensive text for understanding Physical Chemistry with focus on development of problem-solving skill. The purpose of adaptation of this book is to make the learning experience more complete and help students develop a thought process about a given concept and build an aptitude to apply the same to solve a problem. The adaptation adds the distilled teaching expertise of the author to the original text, supplementing it with additional concepts and solved problems at appropriate places based on his experience of learning pattern of the students and obstacles in their learning curve.

A compelling reason for any author to write a book (especially when the author is a teacher too) is to help the student learn using the book without the assistance of a teacher. It has been an enriching journey so far, learning at different levels, as a student, as a teacher and now as an adapting author of this book.

Competitive examinations like the JEE (Main and Advanced) have a knack of testing the fundamental concepts. Thus, a student should learn to solve every question with the most basic and logical approach. There is no substitute for hard work, and thus, a variety of problems are given to master the concepts for the students. At this juncture, I would also like to emphasize the value of discipline when following this book.

This book contains the following key features:

(a) A detailed, relevant, lucid and up to date coverage of the concepts as per the JEE curriculum. Figures, graphs, schematic representations, molecular representations and tables have been suitably inserted to help the student familiarize and understand the practical application of the concepts.

(b) Solved Examples: Ample are provided after important concepts. The students should try to go carefully through these examples as illustrations.

(c) Solved Objective Questions from previous year papers: This section will help the student to get acquainted with the actual JEE questions and to test the skills learnt in the chapter.

(d) Review Questions: This section will help to revise the basic concepts of the chapter. I advise every student to go back and read the concepts for every question, which he/she is not able to solve in this section

(e) Numerical Problems: This section tests the skill level of students to do more challenging subjective problems.

(f) Additional Objective Questions: This section tests the skills of the students to do challenging objective problems as per the latest JEE pattern.

(g) Revision Tests: This is a new feature of the adaptation, comprising of chapter-wise tests based on each chapter, provided at the end of the book (Appendix A). It helps in a holistic revision of all the chapters of Physical Chemistry after the completion of the syllabus for students. It covers all question-types as per JEE requirements and serves as the ultimate revision tool for any JEE candidate

(h) Additional Practice Problems: This is also an additional feature of the adaptation, comprising a selected set of numerical problems arranged chapter-wise at the end of the book (Appendix B). Solving these as part of their revision would equip students to solve any type of problem and approach JEE with confidence.

I hope that the students would benefit from the experience of learning "Physical Chemistry for JEE (MAIN & ADVANCED)". I will be grateful for all the readers (particularly students) for their evaluation, of this book. Their comments, criticism and suggestions will be incorporated in the subsequent editions.

And finally to each and every student, who attempts to read this book, remember,

Every time you try and fail, you are still a step ahead than the person who has not tried. So keep trying!

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I must thank the Almighty for helping me find the right direction of life and the best of people in the form of friends and family. Many people have contributed to this endeavor of making this project a reality. I must express my heartfelt gratitude to my parents for helping me reach where I am today. Many thanks to my wife (who is also my life) Ashwini, for constantly encouraging me to pursue my dreams, having faith in me, pushing me beyond my limits (as per the second law of thermodynamics) and bearing with my analogies of Chemistry for life.

Vipul Mehta

Mumbai

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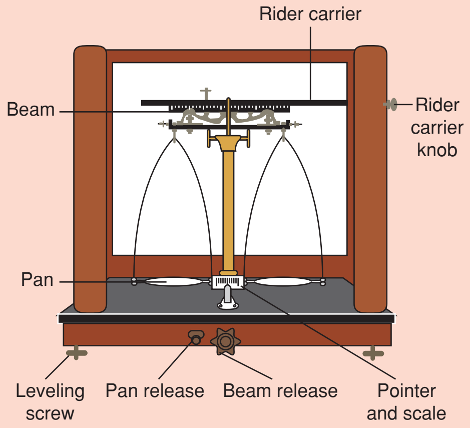
1

Mole Concept–I



A traditional two-pan analytical balance capable of measurements to the nearest 0.0001 g

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Chemistry is the science that deals with the composition, structure and properties of matter; the reactions by which one substance is converted into another; and the energy associated with matter. To understand chemistry, it is important to study matter which is made up of atoms and molecules. This matter is subject to the laws of nature, which originate from reproducible quantitative measurements. Measurements consist of two parts – numbers and specific units. The magnitude and the manipulation of the numbers we use in chemistry from the beginning point of our study.

1.1 | BASIC CONCEPTS

Matter and its Nature

Matter is anything that occupies space and has mass. It is what our universe is made of. All substances that we encounter, whether natural (e.g., trees, ocean, air, people, etc.) or synthetic (e.g., paper, cloth, etc.) are matter. Matter exists in three physical states – solid, liquid and gas.

1. A **solid** is composed of matter where the particles are close together and remain in relatively fixed positions. Movement of the particles is very restricted and confined mostly to vibrations about these positions. Because of the fixed positions of the particles, *solids have a definite shape and a definite volume*.
2. A **liquid** is composed of matter where the particles are close together but are able to move past one another. Because of the movement of the particles, liquids flow and take the shape of the lower part of a container. *Liquids have a definite volume but not a definite shape*.
3. A **gas** is made up of atoms or molecules that are not all close to one another and move independently in all directions with

random motion. The particles in gases fill a container uniformly. *Gases have neither a definite volume nor a definite shape*.

These three states can be converted from one form to the other by altering temperature and pressure. The temperature at which a pure substance changes from one physical state to another is a fundamental and constant physical property. A substance *melts* when it changes from the solid to the liquid state and *freezes* when it changes from the liquid to the solid state. At a higher temperature, the liquid begins to boil. Boiling occurs when bubbles of vapor form in the liquid and rise to the surface. In the reverse process, the change from the gaseous state to the liquid state when it is cooled is known as condensation.

Thousands of distinct kinds of matter exist and can be broadly classified as mixtures and pure substances (Fig. 1.1).

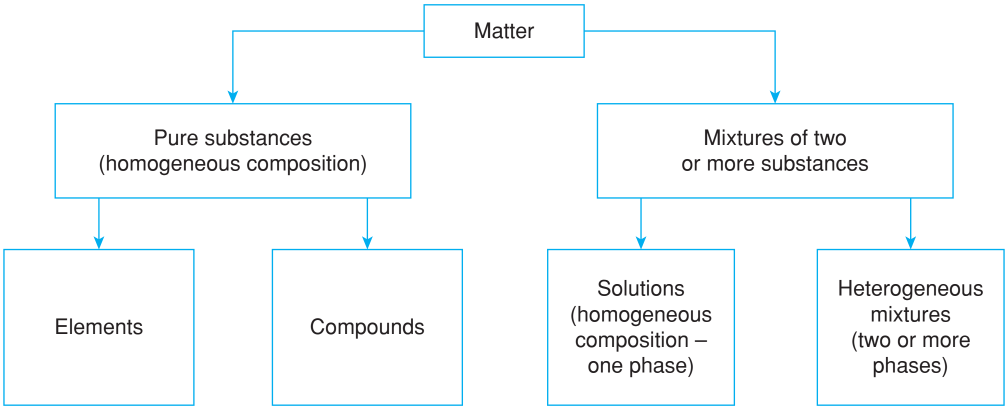

Matter
Pure substances (homogeneous composition)
Mixtures of two or more substances
Elements
Compounds
Solutions (homogeneous composition – one phase)
Heterogeneous mixtures (two or more phases)

Figure 1.1 Classification of matter.

1. **Pure substance** is a particular kind of matter with a definite, fixed composition. Unlike mixtures, the components of pure substances cannot be separated by physical methods; however, they can be separated by chemical methods. These substances can be either elements or compounds.
   - **(a) Elements** are substances that contain only one kind of particles – atoms or molecules. For example, oxygen in the atmosphere, aluminium in aluminium foil, iron in nails, copper in electrical wires, and so on. Elements are the fundamental building blocks from which all other substances are made.

     Imagine cutting a piece of gold metal in half and then repeating this process again and again and again. In theory, we should eventually end up with a single gold atom. If we tried to split this atom in half, we would end up with something that no longer retains any of the properties of gold. An **atom**, in other words, is the smallest particle that can be used to identify an element.
   - **(b) Compounds** are substances that contain more than one element combined in fixed proportions. Water, for example, is composed of the elements hydrogen and oxygen in the ratio of two atoms of hydrogen to one atom of oxygen (Fig. 1.2). If we tried to divide a sample of water into infinitesimally small portions, we would eventually end up with a single molecule of water containing two hydrogen atoms and one oxygen atom. If we tried to break this molecule into its individual atoms, we would no longer have water. A **molecule** is, therefore, the smallest particle that can be used to identify a compound.

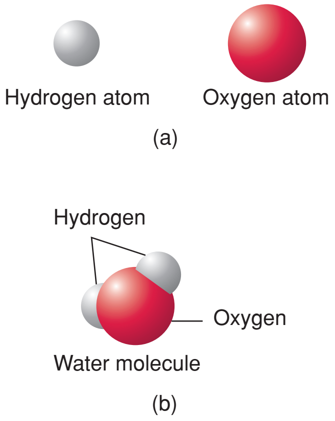


Figure 1.2 Atoms combine to form molecules. Water molecule consists of one oxygen atom and two hydrogen atoms.

Both elements and compounds have a constant composition. Water, for example, is always 88.8% oxygen by weight, regardless of where it is found. No matter where it comes from, salt always contains 1.54 times as much chlorine by weight as sodium. Pure substances also have constant chemical and physical properties. Pure water always freezes at 0°C and boils at 100°C at atmospheric pressure.

It can be seen that a compound contains atoms of an element in fixed ratio, which characterize its physical and chemical properties, making them distinct from its constituting elements. For example, water is liquid whereas its constituents hydrogen and oxygen are gases. Similarly, oxygen is used for combustion, while water acts as a fire extinguisher.

2. **Mixture** is a material containing two or more substances and can be either heterogeneous or homogeneous. Mixtures are variable in composition. If we add a spoonful of sugar to a glass of water, a heterogeneous mixture is formed immediately. The two phases are a solid (sugar) and a liquid (water). But upon stirring, the sugar dissolves to form a homogeneous mixture or solution. Both substances are still present.
   - **(a)** A **homogeneous mixture** is the same throughout and the components disperse uniformly into each other. In a typical homogeneous mixture, the mixing extends all the way to the molecular level. When table salt is added to water, it forms a solution. *A **solution** usually refers to homogeneous mixtures with one liquid phase*. Thus components of a solution cannot be separated by filtration. However, the two components can be separated by a laboratory procedure called *distillation*.
   - **(b)** A **heterogeneous mixture** is a non-uniform mixture containing two or more components where portions of each component are large enough to be detected, although some magnification may be necessary. Oil and water mixture and soil are examples of heterogeneous mixtures. Soil is made up of bits of sand, some black matter, and perhaps pieces of vegetation. One can easily detect several solid phases with the naked eye. Other examples of heterogeneous mixtures are carbonated beverages (liquid and gas) and muddy water (liquid and solid). Heterogeneous mixtures can often be separated into their components by simple laboratory procedures. For example, suspended solid matter can be removed from water by *filtration*. In some cases, centrifugation method is used to separate heterogeneous mixtures.

Solved Example 1-1

Define **(a)** matter, **(b)** element, **(c)** compound, **(d)** mixture, **(e)** homogeneous solution and **(f)** heterogeneous mixture. Label each of the following compounds as a substance, heterogeneous mixture or a solution:
(i) Seawater **(ii)** Phosphorus **(iii)** Air **(iv)** Bromine **(v)** Concrete

Solution

(a) Matter has mass and occupies space.

(b) An element is a pure substance that cannot be decomposed into something simpler.

(c) A compound is a pure substance that is composed of two or more elements in some fixed or characteristic proportion.

(d) Mixtures result from combinations of pure substances in varying proportions.

(e) A homogeneous mixture has one phase. It has the same properties throughout the sample.

(f) A heterogeneous mixture has more than one phase. The different phases have different properties.

The compounds are classified as:
(i) Solution **(ii)** Substance **(iii)** Heterogeneous mixture **(iv)** Substance **(v)** Heterogeneous mixture

Solved Example 1-2

Buckyballs are used in nanotechnology. One type of buckyball has the chemical formula C_{60}. Briefly discuss the classification of buckyballs into elements, atoms, molecules and compounds.

Solution

Buckminster fullerene or buckyball is an allotrope of the element carbon, and is a molecule containing same type of atoms. Thus, it can be classified both as element as well as molecule.

Solved Example 1-3

Identify the following as homogeneous or heterogeneous mixture and suggest a technique for separating their compounds.

(a) Alcohol and water

(b) Chalk and table salt

(c) Pigments in a bucket of paint

Solution

(a) Alcohol and water → Homogeneous mixture

Distillation method is used for separating the components.

(b) Chalk and table salt → Heterogeneous mixture

Filtration method is used for separating the components.

(c) Pigments in a bucket of paint → Heterogeneous mixture

Centrifugation method is used for separating the components.

Solved Example 1-4

What do each of the boxes in Fig. 1.3 represent?

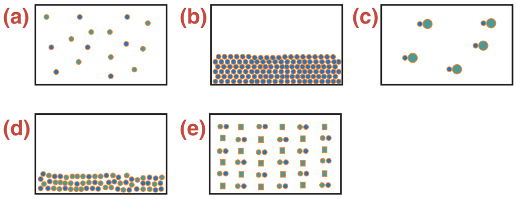


Figure 1.3

Solution

(a) This represents gaseous molecules moving randomly.

(b) This represents solid with tightly packed spheres.

(c) This represents a gaseous compound with atoms and molecules moving randomly.

(d) This represents a heterogeneous mixture of two elements.

(e) This represents a homogeneous mixture of an element and a compound.

Dalton's Atomic Theory

The concept of atoms began nearly 2500 years ago when certain Greek philosophers expressed the belief that matter is ultimately composed of tiny indivisible particles, and it is from the Greek word *atomos*, meaning "not cut", that the word *atom* is derived. At the beginning of the 19th century, John Dalton (1766–1844), an English scientist, used the Greek concept of atoms to make sense out of the laws of conservation of mass and definite proportions. He reasoned that if atoms really exist, they must have certain properties to account for these laws. He described such properties which together constitute the **Dalton's atomic theory:**

1. Matter consists of tiny particles called atoms.
2. In any sample of a pure element, all the atoms are identical in mass and other properties. The atoms of different elements differ in mass and other properties.
3. When atoms of different elements combine to form compounds, new and more complex particles form. However, in a given compound the constituent atoms are always present in the same fixed **numerical** ratio.
4. Atoms are indestructible. In chemical reactions, the atoms rearrange but they do not themselves break apart.

Dalton's theory easily explained the laws of chemical combination as discussed in Section 1.2.

1. **To explain the law of conservation of mass:** According to the theory, a chemical reaction is simply a reordering of atoms from one combination to another. If no atoms are gained or lost and if the masses of the atoms cannot change, then the mass after the reaction must be the same as the earlier mass. This explanation of the law of conservation of mass works so well that it serves as the reason for balancing chemical equations.
2. **To explain the law of definite proportions:** According to the theory, a given compound always has atoms of the same elements in the same numerical ratio. Suppose that two elements, A and B, combine to form a compound in which the number of atoms of A equals those of B (i.e., the *atom ratio* is 1:1). If the mass of a B atom is twice that of an A atom, then every time we encounter a sample of this compound, the mass ratio (A to B) would be 1:2. This same mass ratio would exist regardless of the size of the sample, so in samples of this compound, the elements A and B are always present in the same proportion by mass.

Solved Example 1-5

What assumption of Dalton was known to be an error?

Solution

Dalton's assumption that all atoms of the same element are identical in mass is an error. For example, it is possible for atoms of the same element to have a different number of neutrons and hence different masses.

Solved Example 1-6

How was Dalton's atomic theory able to explain the law of conservation of mass?

Solution

According to the theory, a chemical reaction is simply a reordering of atoms from one combination to another. If no atoms are gained or lost and if the masses of the atoms cannot change, then the mass after the reaction must be the same as the earlier mass.

Concept of Atom, Molecule, Element and Compound

While discussing pure substances, we had introduced the terms atoms, molecules, elements and compounds. In this section, we understand their composition which affects their physical and chemical properties.

Atoms combine to form molecules. It can be seen that a compound contains atoms of an element in fixed ratio, which characterize its physical and chemical properties, making them distinct from its constituting elements. **Atomicity** for an elementary substance is defined as the number of atoms in a molecule of an element. For example, water molecule consists of one oxygen atom and two hydrogen atoms. where water is liquid whereas its constituents hydrogen and oxygen are gases. Similarly, oxygen is used for combustion, while water acts as a fire extinguisher.

Properties, that is, the characteristics of substances are classified as either physical or chemical.

1. **Physical properties** are the in-built characteristics of a substance that can be determined without altering its composition; they are associated with its physical existence. Common physical properties include color, taste, odor, states of matter (solid, liquid or gas), density, melting point and boiling point. For example, a physical property is the ability of a substance (such as water) to get converted into different physical states (such as water vapor and ice) without changing its composition.
2. **Chemical properties** describe the ability of a substance to form new substances, either by reaction with other substances or by decomposition. For example, a chemical property of the element iron is its tendency to react with oxygen from the air in the presence of water to form rust (a compound composed of iron and oxygen). The conversion of rust back into iron and oxygen is a difficult chemical process. In some cases, chemical properties relate to the absence of specific changes. For example, a chemical property of the element gold is that it maintains its lustrous appearance because it resists rusting or tarnishing.

Another way of classifying a property is according to whether or not it depends on the size of the sample under study.

1. **Extensive property:** A property that depends on the size. For example, two different pieces of gold can have different volumes, but both have the same characteristic shiny yellow color and both will begin to melt if heated to same temperature. Volume is said to be an extensive property.
2. **Intensive property:** A property that is independent of sample size. For example, color, freezing point, and boiling point are examples of intensive physical properties that can help us identify substances. Chemical properties are also intensive properties and also can be used for identification.

For identification purposes, intensive properties are more useful than extensive ones because every sample of a given substance exhibits the same set of intensive properties.

Solved Example 1-7

Identify the following as either a physical or a chemical property.

(a) Diamond is one of the hardest known substances.
(b) Carbon monoxide is a poisonous gas.
(c) Soap is slippery.
(d) Silver tarnishes.
(e) Gold does not rust.
(f) Carbon dioxide freezes at –78°C.
(g) Tin is a shiny, gray metal.
(h) Sulphur burns in air.
(i) Aluminium has a low density.

Solution

Physical properties are characteristic properties possessed by substances. A physical property can be measured and used to characterize a pure substance without reference to other substances. A chemical property governs the reactivity of a substance either with other substances or to give other substances.

(a) physical; **(b)** chemical; **(c)** physical; **(d)** chemical; **(e)** chemical; **(f)** physical; **(g)** physical; **(h)** chemical; **(i)** physical

---

Solved Example 1-8

What is smallest particle used to identify **(a)** an element and **(b)** a compound?

Solution

(a) Atom is the smallest particle used to identify an element.

(b) Molecule is the smallest particle used to identify a compound.

Representation of Physical Quantities

An important step in the scientific method is observation. In general, observations fall into two categories – qualitative and quantitative. **Qualitative observations**, such as the color of a chemical or that a mixture becomes hot when a reaction occurs, do not involve numerical information and are usually of limited value. More important are **quantitative observations**, or **measurements**, which yield numerical data. In chemistry, we make various measurements that aid us in describing both chemical and physical properties. Both the **number** and the **unit** are essential parts of the measurement, because the unit gives the reported value a sense of size. For example, if you were told that the distance between two points is 25, you would naturally ask "25 what?" The distance could be 25 inches, 25 meters, 25 kilometers, or 25 of any other unit that is used to express distance. A number without a unit is really meaningless.

A **measurement** determines the quantity, dimensions or extent of something, usually in comparison to a specific unit. A **unit** is a definite quantity adopted as a standard of measurement. Thus, a measurement (e.g., 1.23 meters) consists of two parts: a numerical quantity (1.23) followed by a specific unit (meters). However, measurements can be inexact; they contain **uncertainties** (also called **errors**). One source of uncertainty is associated with limitations in our ability to read the scale of the measuring instrument. Uncontrollably changing conditions at the time of the measurement can also cause errors that are more important than scale reading errors. For example, if you are measuring a length of wire with a ruler, you may not be holding the wire perfectly straight every time.

Scientific Notation

Scientists often use numbers that are very large or very small in measurements. For example, the earth's age is estimated to be about 4,500,000 (4.5 billion) years or mass of a hydrogen atom is estimated to be 0.0000000000000000000000 0167. Numbers like these are bulky to write, so to make them more compact scientists use powers of 10. Writing a number as the product of a number between 1 and 10 multiplied by 10 raised to some power is called **scientific notation**.

To learn how to write a number in scientific notation, let us consider the number 24989. To write this number in scientific notation:

1. Move the decimal point in the original number so that it is located after the first non-zero digit.

$$\underline{24989 \rightarrow 2.4989} \text{ (decimal moves four places to the } \textbf{left}\text{)}$$

2. Multiply this new number by 10 raised to the proper exponent (power). The proper exponent is equal to the number of places that the decimal point was moved.

$$2.4989 \times 10^4$$

3. The sign on the exponent indicates the direction the decimal was moved.

Positive exponent (like in the above case) indicates decimal was moved to the **left**

Negative exponent indicates decimal was moved to the **right**

We follow the same rules as exponents according to the kinds of arithmetic being performed.

1. **Multiplication and division:** For multiplying and dividing two scientific notations, the numerals are multiplied or divided, while the exponents are added or subtracted. For example, the product of 2.25×10^{-4} and 3.25×10^{-6} would be

$$(2.25 \times 3.25) \times 10^{-4+(-6)} = 7.3125 \times 10^{-10}$$

Similarly on dividing 2.25×10^{-4} by 3.25×10^{-6}, we get

$$(2.25 \div 3.25) \times 10^{-4-(-6)} = 0.6923 \times 10^{2}$$

2. **Addition and subtraction:** For adding or subtracting two numbers, the exponents must be made same, so that they can be taken out as a common factor. For example, to obtain the sum of 2.25×10^{-4} and 3.25×10^{-6}, we make the exponents same as follows:

$$225 \times 10^{-6} + 3.25 \times 10^{-6}$$

or

$$2.25 \times 10^{-4} + 0.0325 \times 10^{-4}$$

So, the common factor 10^{-6} or 10^{-4} can be taken out, and the sum can be calculated as

$$(225 + 3.25) \times 10^{-6} = 228.25 \times 10^{-6} = 2.2825 \times 10^{-4}$$

or

$$(2.25 + 0.0325) \times 10^{-4} = 2.2825 \times 10^{-4}$$

Hence, we can see that the two ways of addition essentially give the same sum. Similarly, for subtraction, the exponents are first made same, and then the difference is calculated.

$$(225 - 3.25) \times 10^{-6} = 221.75 \times 10^{-6} = 2.2175 \times 10^{-4}$$

or

$$(2.25 - 0.0325) \times 10^{-4} = 2.2175 \times 10^{-4}$$

Solved Example 1-9

Express the following numbers in scientific notation (one digit to the left of the decimal point): **(a)** 157, **(b)** 0.157, **(c)** 0.0300, **(d)** 40,000,000 (two significant figures), **(e)** 0.0349, **(f)** 32,000, **(g)** 32 billion, **(h)** 0.000771, **(i)** 2340.

Solution

(a) 1.57×10^{2}; **(b)** 1.57×10^{-1}; **(c)** 3.00×10^{-2}; **(d)** 4.0×10^{7}; **(e)** 3.49×10^{-2}; **(f)** 3.2×10^{4}; **(g)** 3.2×10^{10}; **(h)** 7.71×10^{-4}; **(i)** 2.34×10^{3}

Precision and Accuracy

Two terms often used in reference to measurements are *accuracy* and *precision*. **Accuracy** refers to how close a measurement is to the true or correct value. **Precision** refers to how closely repeated measurements of a quantity come to each other and to the average. Notice that the two terms are not equivalent, because the average does not always correspond to the true or correct value.

For measurements to be accurate**,** the measuring device must be carefully calibrated (adjusted) so it gives correct values when a standard reference is used with it. For example, to calibrate an analytical balance, a known reference mass is placed on the balance and a calibration routine within the balance is initiated. Once calibrated, the balance will give correct readings, the accuracy of which is determined by the accuracy of the standard mass used. Standard reference masses (also called “weights”) can be purchased from scientific supply companies. For measurements to be **precise**, the uncertainty (i.e., the “plus or minus” part of the measurement) should be smaller.

We usually assume that a very precise measurement is also of high accuracy. We can be wrong, however, if our instruments are improperly calibrated. For example, an improperly marked ruler might yield measurements which vary by a hundredth of a centimeter (±0.01 cm), but all the measurements would be too large by 1 cm. Hence, this improperly marked ruler will yield measurements that are each wrong by one whole unit. The measurements might be precise, but the accuracy would be very poor.

Solved Example 1-10

An improperly marked ruler yielded measurements which vary by a hundredth of a centimeter (±0.01 cm). Would the measurements taken by the ruler be accurate or precise?

Solution

All the measurements would be too large by 1 cm. Thus, the measurements taken would be precise with ±0.01 cm. However, since the ruler is not calibrated properly, the measurements are not accurate. For properly calibrated instruments, a very precise measurement is also of high accuracy.

Solved Example 1-11

Consider the following three archery targets in Fig. 1.4:

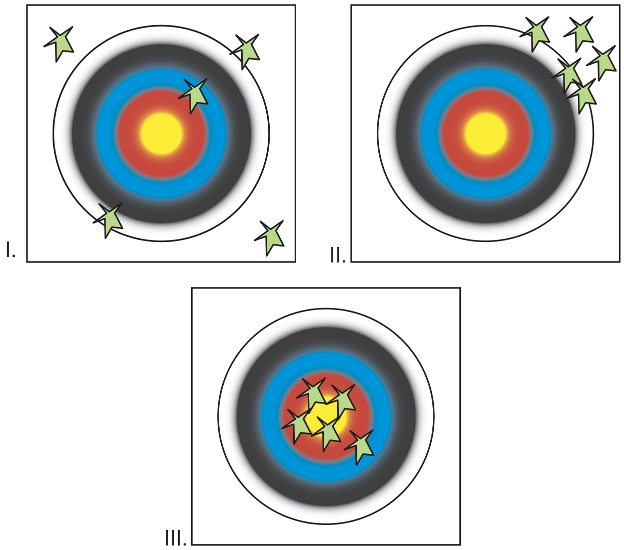


Figure 1.4

Which figure(s) represent a result having high precision?

Solution

Both Figures II and III have large number of archery marks concentrated at one region, so they are highly precise. However, Figure III has density of dots closer to the target, so it is more accurate.

Significant Figures

Significant figures (*or* **significant digits**) are digits in a number that results from a measurement which are known with certainty. Since all measurements involve uncertainty, we must use the proper number of significant figures in each measurement. The uncertainty in a measurement is denoted by writing the digits known for sure *plus* one that is estimated. For example, consider the following two temperature measurements, the first measurement, 24.3°C, has three significant figures; the second, 24.32°C, has four significant figures.

Rules for Counting Significant Figures

Rule 1: All **non-zero digits are significant**. For example, in the two temperature measurements discussed above to understand uncertainty, the first measurement, 40.2°C, has three significant figures; and the second, 40.23°C, has four significant figures.

Rule 2: All **zeros between non-zero digits are significant**. For example,

204 has three significant figures (2, 0, 4)
3.06 has three significant figures (3, 0, 6)
62.08 has four significant figures (6, 2, 0, 8)

Rule 3: All **zeros at the end of a number that includes a decimal point are significant**. For example,

0.400 has three significant figures (4, 0, 0)
4.00 has three significant figures (4, 0, 0)
40 has two significant figures (4, 0)

However, **zeros at the end of a number *without* a decimal point are *not significant***. For example,

9000 has one significant figure (9)
590 has two significant figures (5, 9)

Rule 4: All **zeros before the first non-zero digit are *not significant***. These zeros are used to locate a decimal point:

0.0035 has two significant figures (3, 5)
0.0208 has three significant figures (2, 0, 8)

Rule 5: Some numbers are called **exact numbers** and **have an infinite number of significant figures**. Exact numbers occur in simple counting operations; when you count Rs. 25, you have exactly Rs. 25. Exact numbers have no uncertainty. These are represented by placing as many zeros as possible after the number and the decimal point, such as 25.0000.

These rules are applied in case of arithmetic operations, such as multiplication, division, addition and subtraction as follows.

1. **For addition and subtraction:** The answer should have the same number of decimal places as the quantity with the fewest number of decimal places. For example, consider the following addition of measured quantities.

$$\begin{array}{r l} 3.247 & \\ 41.36 & \\ +125.2 & \longleftarrow \text{(This number has only 1 decimal place.)} \\ \hline 169.8 & \longleftarrow \text{(This answer has been rounded to 1 decimal place.)} \end{array}$$

In this calculation, the digits beneath the 6 and the 7 are unknown; they could be anything. (They are not necessarily zeros because if we *knew* they were zeros, then zeros would have been written there.) Adding an unknown digit to the 6 or 7 will give an answer that is also unknown, so for this sum we are not justified in writing digits in the second and third places after the decimal point. Therefore, we round the answer to the nearest tenth.

2. **For multiplication and division:** The number of significant figures in the answer should not be greater than the number of significant figures in the least precise measurement. Let us look at a typical problem involving some measured quantities.

$$\frac{\overset{\text{3 Significant figures}}{\searrow\, 3.14} \times \overset{\text{4 Significant figures}}{2.751 \,\swarrow}}{\underset{\text{2 Significant figures}}{\nearrow\, 0.64}} = 13$$

The result displayed on a calculator is 13.49709375. However, the least precise factor, 0.64, has only two significant figures, so the answer should have only two. The correct answer, 13, is obtained by rounding off the calculator answer.

Solved Example 1-12

What is the difference between 5.0 g and 5.00 g?

Solution

The difference is that 5.0 g has two significant digits and 5.00 g has three significant digits; and 5.0 g has less precise measurement than 5.00 g because it has less number of significant digits.

Limiting the Result by Rounding Off the Value

When we do calculations on a calculator, we often obtain answers that have more digits than are justified. It is, therefore, necessary to remove the excess digits in order to express the result by limiting it to proper number of significant figures. When digits are removed from a number, the value of the last digit retained is determined by a process known as **rounding off numbers**. The rules for rounding off numbers in order to limit the result are as follows:

Rule 1: When the first digit after those you want to retain is 5 or greater, that digit and all others to the right are removed and the last digit retained is increased by one. The following examples are rounded off to four significant digits:

$1.026\underline{868} = 1.027$

These three digits are removed.

This digit is changed to 7.

$18.02\underline{500} = 18.03$

These three digits are removed.

This digit is changed to 3.

$12.\underline{89}9 = 12.90$

This digit is removed.

These two digits are changed to 90.

Rule 2: When the first digit after those you want to retain is 4 or less, that digit and all others to its right are removed. The last digit retained is not changed. The following examples are rounded off to four significant digits:

$74.693 = 74.69$

This digit is removed.

$1.006\underline{29} = 1.006$

These two digits are removed.

Rule 3: When the first digit after those you want to retain is 5, that digit and all others to its right are removed. The last digit retained is not changed if it is an even number and increased by 1 if it is an odd number. The following examples are rounded off to four significant digits:

$1.024\underline{568} = 1.024$

These three digits are removed.

This digit is retained.

$18.03\underline{500} = 18.04$

These three digits are removed.

This digit is changed to 4.

Solved Example 1-13

Perform the following arithmetic and round off the answers to the correct number of significant figures. Include the correct units with the answers.

(a) 0.0023 m × 315 m

(b) 84.25 kg – 0.01075 kg

(c) $\dfrac{(184.45\ \text{g} - 94.45\ \text{g})}{(31.4\ \text{mL} - 9.9\ \text{mL})}$

(d) $\dfrac{23.4\ \text{g} + 102.4\ \text{g} + 0.003\ \text{g}}{6.478\ \text{mL}}$

(e) (313.44 cm – 209.1 cm) × 8.2234 cm

Solution

(a) 0.72 m^2; **(b)** 84.24 kg; **(c)** 4.2 g mL^{-1}; **(d)** 19.42 g mL^{-1}; **(e)** 857.7 cm^2.

Solved Example 1-14

An electronic balance used in the mailroom displays tenths of a kilogram from 0 to 140 kg. How many significant figures should be used to express the mass of any package whose mass is between 80.2 and 83.5 kg.?

Solution

Since there are 3 significant digits in 80.2 and 83.5 so the answer should also contain 3 significant digits.

Solved Example 1-15

What is the result when the expression, 412.272 + 0.00031 – 1.00797 + 0.000024 + 12.8 is evaluated?

Solution

The sum obtained after calculation is 424.06458. After rounding off, we get the result as 424.1 with 4 significant digits.

The International System of Units (S.I.)

In science, and in every industrialized nation on the earth, metric-based units are used. The advantage of working with metric units is that converting to larger or smaller units can be done simply by moving a decimal point, because metric units are related to each other by simple multiples of 10. Besides, it has one unit of measurement for each physical quantity and scalability by prefixes. However, it was important that a common system be devised for use across the world.

In 1960, a simplification of the original metric system was adopted by the 11th General Conference on Weights and Measures (an international body). It is called the International System of Units, abbreviated **S.I.** from the French name, *Le Système International d'Unités*. The S.I. is now the dominant system of units in science and engineering, although there is still some usage of older metric units.

As its foundation, the S.I. has a set of **base units** (Table 1.1) for seven measured quantities.

Table 1.1 The S.I. base units

Measurement	Unit	Symbol	Description
Length (l)	meter	m	The distance traveled by light during a precisely specified time interval.
Mass (m)	kilogram	kg	A platinum–iridium standard mass kept near Paris. For measurements on an atomic scale, the atomic mass unit, defined in terms of the atom carbon-12, is usually used.
Time (s)	second	s	The oscillations of light emitted by an atomic (caesium-133) source. Accurate time signals are sent worldwide by radio signals keyed to atomic clocks in standardizing laboratories.
Electric current (I)	ampere	A	The constant current which, if maintained in two straight parallel conductors of infinite length, of negligible circular cross-section, and placed 1 m apart in vacuum, would produce between these conductors a force equal to 2×10^{-7} newton per meter of length.
Temperature (T)	kelvin	K	The fraction 1/273.16 of the thermodynamic temperature of the triple point of water.
Amount of substance (n)	mole	mol	The amount of substance of a system which contains as many elementary entities as there are atoms in 0.012 kilogram of carbon-12
Luminous intensity (I_v)	candela	cd	The luminous intensity, in a given direction, of a source that emits monochromatic radiation of frequency 540×10^{12} hertz and that has a radiant intensity in that direction of 1/683 watt per steradian.

The prefixes commonly used in S.I. units are shown in Table 1.2.

Table 1.2 Common prefixes and numerical values for S.I. units

Prefix	Symbol	Numerical value	Power of 10 equivalent
yotta	Y	1,000,000,000,000,000,000,000,000	10^{24}
zeta	Z	1,000,000,000,000,000,000,000	10^{21}
exa	E	1,000,000,000,000,000,000	10^{18}
peta	P	1,000,000,000,000,000	10^{15}
tera	T	1,000,000,000,000	10^{12}
giga	G	1,000,000,000	10^{9}
mega	M	1,000,000	10^{6}
kilo	k	1,000	10^{3}
hecto	h	100	10^{2}
deka	da	10	10^{1}
–	–	1	10^{0}
deci	d	0.1	10^{-1}
centi	c	0.01	10^{-2}
milli	m	0.001	10^{-3}
micro	μ	0.000001	10^{-6}
nano	n	0.000000001	10^{-9}
pico	p	0.000000000001	10^{-12}
femto	f	0.000000000000001	10^{-15}
atto	a	0.000000000000000001	10^{-18}
zepto	z	0.000000000000000000001	10^{-21}
yocto	y	0.000000000000000000000001	10^{-24}

The prefixes most commonly used in chemistry are shown in bold.

Solved Example 1-16

Which physical quantities do the following units represent?

(a) Parallactic second **(b)** Solar day
(c) Lunar month **(d)** Leap year

Solution

(a) Parallactic second is not the unit of time. It is a unit of distance corresponding to a parallex of one second of arc and is abbreviated parsec 1 Parsec = 3.08×10^{16} m = 3.26 light years.

(b) Solar day represents the time which elapses between two successive returns of the Sun to the local meridian.

(c) Lunar month represents the time between two full moons or two new moons.

(d) Leap year represents the year in which additional day is added to synchronize it with seasonal year.

Solved Example 1-17

Which of the following are base units and which are derived?

(a) dyne **(b)** newton **(c)** ampere
(d) square centimeter **(e)** candela

Solution

(a) Derived. It is a CGS unit for force.

(b) Derived. It is a S.I. derived unit for force.

(c) Base. It is an S.I. base unit for current.

(d) Derived. It is a S.I. derived unit for area.

(e) Base. It is an S.I. base unit for luminous intensity.

Physical Quantities and Their Measurements

Mass and Weight

Although we often use mass and weight interchangeably in our everyday lives, they have quite different meanings in chemistry. In science we define the **mass** of an object as the amount of matter in the object. Mass is measured on an instrument called a balance. The **weight** of an object is a measure of the effect of gravity on the object. Weight is determined by using an instrument called a scale, which measures force against a spring. This means mass is independent of the location of an object, but weight is not.

Mass is measured by comparing the weight of a sample with the weights of known standard masses. The operation is called **weighing**, and the apparatus used is called a **balance** (Fig. 1.5). The sample is placed on the left pan and some standard masses are added to the right pan. When the weight of the sample and the total weight of the standards match each other, their masses are then equal.

In the S.I., the base unit for mass is the **kilogram (kg)**, although the **gram (g)** is a more conveniently sized unit for most laboratory measurements. One gram, of course, is 1/1000 of a kilogram (1 kilogram = 1000 g, so 1 g must equal 0.001 kg).

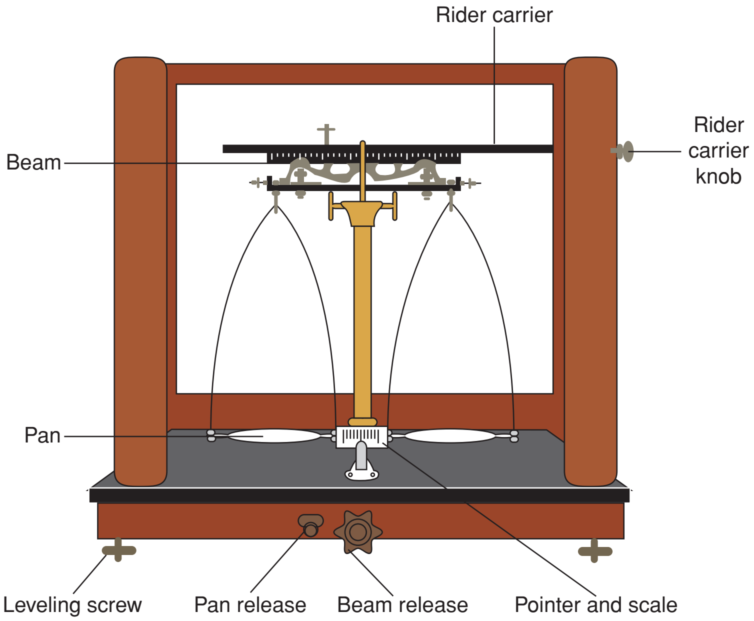


Figure 1.5 A traditional two-pan analytical balance capable of measurements to the nearest 0.0001 g.

Volume

Volume is a derived unit with dimensions of (length)^3. With these dimensions expressed in meters, the derived S.I. unit for volume is the **cubic meter, m^3**. In chemistry, measurements of volume usually arise when we measure amounts of liquids. Some commonly used laboratory apparatus used for measuring volume are given in Fig. 1.6. Graduated cylinders are used to measure volumes to the nearest milliliter. Precise measurements of volume are made using burets, pipets, and volumetric flasks.

The traditional metric unit of volume used for this is the **liter (L)**. In S.I. terms, a liter is defined as exactly 1 cubic decimeter.

$$1\ \mathrm{L} = 1000\ \mathrm{dm}^3$$

However, even the liter is too large to conveniently express most volumes measured in the lab. The glassware we normally use, such as that illustrated in Fig. 1.6, is marked in **milliliters (mL)**.

$$1\ \mathrm{L} = 1000\ \mathrm{mL}$$

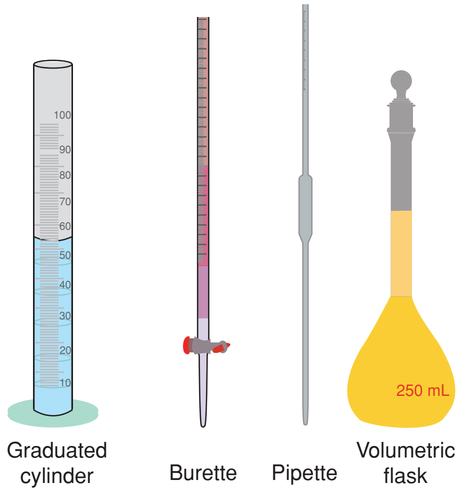


Figure 1.6 Laboratory apparatus measuring volume.

Because 1 dm = 10 cm, then $1\ \text{dm}^3 = 1000\ \text{cm}^3$. Therefore, 1 mL is exactly the same as $1\ \text{cm}^3$.

$$1\ \text{cm}^3 = 1\ \text{mL}$$
$$1\ \text{L} = 1000\ \text{cm}^3 = 1000\ \text{mL}$$

Density

Density is defined as the ratio of an object's mass to its volume. Density (ρ) is a physical characteristic of a substance and may be used as an aid to its identification. When the density of a solid or a liquid is given, the mass is usually expressed in grams and the volume in milliliters or cubic centimeters.

$$\rho = \frac{\text{Mass}}{\text{Volume}} = \frac{\text{g}}{\text{mL}} \quad \text{or} \quad \rho = \frac{\text{g}}{\text{cm}^3}$$

The S.I. units of density is the ratio of the S.I. units of mass and volume, and is given by kg m^{-3}.

Each pure substance has its own characteristic density (Table 1.3). Gold, for instance, is much more dense than iron. Each cubic centimeter of gold has a mass of 19.3 g, so its density is $19.3\ \text{g cm}^{-3}$. By comparison, the density of water is $1.00\ \text{g cm}^{-3}$ and the density of air at room temperature is about $0.0012\ \text{g cm}^{-3}$. There is more mass in $1\ \text{cm}^3$ of gold than in $1\ \text{cm}^3$ of iron.

Table 1.3 Densities of some common substances in g cm^{-3} at room temperature

Substance	Water	Aluminium	Iron	Silver	Gold	Glass	Air
Density	1.00	2.70	7.86	10.5	19.3	2.2	0.0012

Since the volume of a substance (especially liquids and gases) varies with temperature, it is important to state the temperature along with the density. For example, the volume of 1.0000 g of water at 4°C is 1.0000 mL; at 20°C, it is 1.0018 mL and at 80°C, it is 1.0290 mL. Density, therefore, also varies with temperature. Most substances, such as the mercury in the bulb of a thermometer, expand slightly when they are heated, so the amount of matter packed into each cubic centimeter is less. Therefore, density usually decreases slightly with increasing temperature. For solids and liquids the size of this change is small, as you can see from the data for water in Table 1.4.

Table 1.4 Density of water as a function of temperature

Temperature (°C)	10	15	20	25	30
Density of water (g cm^{-3})	0.999700	0.999099	0.998203	0.997044	0.995646

Temperature

Temperature is usually measured with a thermometer. Thermometers are graduated in *degrees* according to one of two temperature scales. Both scales use as reference points the temperature at which water freezes and the temperature at which it boils. On the **Celsius scale** water freezes at 0°C and boils at 100°C (Fig. 1.7) On the **Fahrenheit scale**, water freezes at 32°F and boils at 212°F. The S.I. unit of temperature is the **kelvin (K)**, which is the degree unit on the **Kelvin temperature scale**.

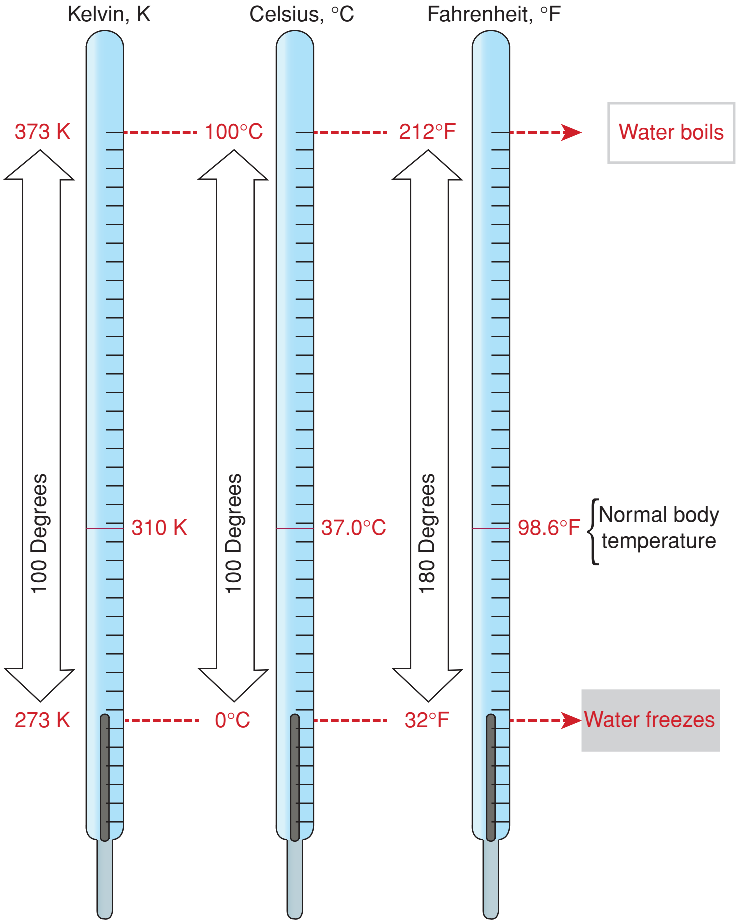


Figure 1.7 Comparison among Kelvin, Celsius and Fahrenheit temperature scales.

Figure 1.7 shows how the Kelvin, Celsius, and Fahrenheit temperature scales relate to each other. It can be seen that on the Celsius scale, there are 100 degree units between the freezing and boiling points of water, while on the Fahrenheit scale this same temperature range is spanned by 180 degree units. Consequently, 5 Celsius degrees are the same as 9 Fahrenheit degrees. We can use the following equation as a tool to convert between these temperature scales.

$$T_F = \left(\frac{9°\text{F}}{5°\text{C}}\right)T_C + 32°\text{F} \tag{1.1}$$

In this equation, T_F is the Fahrenheit temperature and T_C is the Celsius temperature. The 32°F is added to account for the fact that the freezing point of water (0°C) occurs at 32°F on the Fahrenheit scale.

Notice that the kelvin is *exactly* the same size as the Celsius degree. *The only difference between these two temperature scales is the zero point.* The zero point on the Kelvin scale is called **absolute zero** and corresponds to nature's coldest temperature. So, negative temperature is not possible, unlike in Celsius scale. It is 273.15 degree units below the zero point on the Celsius scale, which means that 0°C equals 273.15 K, and 0 K equals –273.15°C. Thermometers are never marked with the Kelvin scale, so to convert from Celsius to Kelvin temperatures, the following equation applies:

$$T_K = (T_C + 273.15°\text{C})\left(\frac{1\ \text{K}}{1°\text{C}}\right) \tag{1.2}$$

This amounts to simply adding 273.15 to the Celsius temperature to obtain the Kelvin temperature. Often, we are given Celsius temperatures rounded to the nearest degree, in which case we round 273.15 to 273. Thus, 25°C equals (25 + 273) K or 298 K.

Solved Example 1-18

A sample of nickel weighs 6.5425 g and has a density of 8.8 g cm^{-3}. What is the volume? Report the answer to correct decimal place.

Solution

Given that mass of the nickel sample, m = 6.5425 g, density of nickel, d = 8.8 g cm^{-3}. Let the volume of the sample be V. Now using the relation for density, $d = m/V$, we get

$$V = \frac{m}{d} = \frac{6.5425\text{ g}}{8.8\text{ g cm}^{-3}} = 0.74\text{ cm}^3$$

Solved Example 1-19

The water level in a metric measuring cup is 0.75 L before the addition of a pebble weighing 150 g. The water level after submerging the pebble is 0.82 L. Determine the density of the pebble in g mL^{-1}.

Solution

The volume displaced by the pebble = 0.82 – 0.75 = 0.07 L = 70 mL.

Mass of the pebble = 150 g.
Therefore, density of the pebble is

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}} = \frac{150}{70} = 2.14\text{ g mL}^{-1}$$

Solved Example 1-20

In a recent accident, some drums of uranium hexafluoride were lost in the ocean containing cold water of about 17°C. The melting point of uranium hexafluoride is 148°F. In what physical state is the uranium hexafluoride in these drums?

(a) solid
(b) liquid
(c) gas
(d) a mixture of solid and liquid

Solution

First, we convert 17°C to Fahrenheit temperature.

$$T_F = \frac{9}{5} \times (17) + 32 = 62.6°\text{F}$$

This temperature is well below the melting point of uranium, so the state of UF_6 in these drums is solid.

Solved Example 1-21

On a new temperature scale (°Z), water boils at 120.0°Z and freezes at 40.0°Z. Calculate the normal human body temperature using this temperature scale.

Solution

Given that 0°C = 120.0°Z and 100°C = 40.0°Z. For the range of freezing of water to boing of water, the temperature range in °Z = 120 – 40 = 80°F.

For 1°Z, the temperature in $°\text{C} = \frac{100}{80} = 1.25°\text{C}$

The normal body temperature for humans is 37°C. So, the same reading in °Z is $\frac{37}{1.25} = 29.6°\text{Z}$ above freezing temperature.

Therefore, body temperature = 29.6 + 40 = 69.6°Z

Dimensional Analysis

After analyzing a problem and collecting the necessary information to solve it, the next step is working the problem to obtain the result. For numerical problems, scientists usually use a system called the **factor label method** or **unit factor method** or **dimensional analysis** to help perform the correct arithmetic operations. In these methods, we treat a numerical problem as one involving a conversion of units from one kind to another. To do this, we use one or more *conversion factors* to change the units of the given quantity to the units of the result.

$$\text{(Given quantity)} \times \text{(Conversion factor)} = \text{(Desired quantity)} \tag{1.3}$$

A **conversion factor** *is a fraction formed from a valid relationship or equality between units and is used to switch from one system of measurement and units to another.* For instance, suppose we want to express a person's height of 72.0 inches in centimeters. To do this, we need the relationship between the inch and the centimeter.

$$1\ \text{in.} = 2.54\ \text{cm}$$

By dividing both sides by 1 in., we get

$$1 = \frac{2.54\ \text{cm}}{1\ \text{in.}}$$

This is the conversion factor which is 2.54 cm/1 in. It is also called unit factor as its value is equal to 1. Conversely, on dividing both sides by 2.54 cm, we get another conversion factor (or unit factor) as 1 in./2.54 cm. On multiplying any quantity by these unit factors, its magnitude would not change as such, only, the units would change. Thus, we can express 72 in. in terms of centimeter as

$$72\ \text{in.} \times \frac{2.54\ \text{cm}}{1\ \text{in.}} = 182.88\ \text{cm} = 183\ \text{cm}$$

Notice that we have canceled the unit inches. The only unit left is centimeters, which is the unit we want for the answer. The result, therefore, is the person's height in centimeters.

Note: Units behave just as numbers do in mathematical operations; this is a key part of the factor-label method. One of the benefits of the factor-label method is that it often lets you know when you have done the wrong arithmetic. It lets us know we have the wrong answer because the units are wrong!

Solved Example 1-22

Use the factor label method to perform the following conversions: **(a)** 3.00 yd to inches, **(b)** 1.25 km to centimeters, **(c)** 3.27 mm to feet, and **(d)** 20.2 miles $(\text{gallon})^{-1}$ to kilometers $(\text{liter})^{-1}$.

Solution

(a) We know that 3 ft = 1 yd and 12 inches = 1 ft. Therefore,

$$3.00\ \text{yd} \times \frac{3\ \text{ft}}{1\ \text{yd}} \times \frac{12\ \text{in.}}{1\ \text{ft}} = 108\ \text{in.}$$

(b) We know that 1 km = 1000 m and 1 m = 100 cm, therefore,

$$1.25\ \text{km} \times \frac{1000\ \text{m}}{1\ \text{km}} \times \frac{100\ \text{cm}}{1\ \text{m}} = 1.25 \times 10^5\ \text{cm}$$

(c) We know that 10 mm = 1 cm; 2.54 cm = 1 in. and 12 in. = 1 ft. Therefore,

$$3.27\ \text{mm} \times \frac{1\ \text{cm}}{10\ \text{mm}} \times \frac{1\ \text{in.}}{2.54\ \text{cm}} \times \frac{1\ \text{ft}}{12\ \text{in.}} = 0.0107\ \text{ft}$$

(d) We know that 1 mile = 1.609 km and 1 gallon = 3.785 L, therefore,

$$20.2 \frac{\text{miles}}{\text{gallon}} \times \frac{1.609\ \text{km}}{1\ \text{mile}} \times \frac{1\ \text{gallon}}{3.785\ \text{L}} = 8.59\ \text{km L}^{-1}$$

Solved Example 1-23

Use the factor-label method to convert an area of 124 ft^2 to square meters. (Hint: What relationships would be required to convert feet to meters?)

Solution

An area of 124 ft^2 is converted in the following way:

$$124\left(\frac{30.48}{1}\right)^2\left(\frac{1}{100}\right)^2 = 11.5\ \text{m}^2$$

Solved Example 1-24

Silver has a density of 10.5 g cm^{-3}. Express this as an equivalence between mass and volume for silver. Write two conversion factors that can be formed from this equivalence for use in calculations. Perform the following conversions.

(a) 32.0 dm s^{-1} to km h^{-1}

(b) 8.2 mg mL^{-1} to μg L^{-1}

(c) 75.3 mg to kg

(d) 137.5 mL to L

(e) 0.025 L to mL

(f) 342 pm^2 to dm^2

Solution

Given that 10.5 g silver = 1 cm^3 silver. Therefore,

$$\frac{10.5\ \text{g Ag}}{1\ \text{cm}^3} \quad \text{and} \quad \frac{1\ \text{cm}^3}{10.5\ \text{g Ag}}$$

(a) $$(32.0\ \text{dm s}^{-1})\left(\frac{1\ \text{m}}{10\ \text{dm}}\right)\left(\frac{1\ \text{km}}{1000\ \text{m}}\right)\left(\frac{3600\ \text{s}}{1\ \text{h}}\right) = 11.5\ \text{km h}^{-1}$$

(b) $$(8.2\ \text{mg mL}^{-1})\left(\frac{1\ \text{g}}{1000\ \text{mg}}\right)\left(\frac{1\times10^6\ \mu\text{g}}{1\ \text{g}}\right)\left(\frac{1000\ \text{mL}}{1\ \text{L}}\right) = 8.2\times10^6\ \mu\text{g L}^{-1}$$

(c) $$(75.3\ \text{mg})\left(\frac{1\ \text{g}}{1000\ \text{mg}}\right)\left(\frac{1\ \text{kg}}{1000\ \text{g}}\right) = 7.53\times10^{-5}\ \text{kg}$$

(d) $$(137.5\ \text{mL})\left(\frac{1\ \text{L}}{1000\ \text{mL}}\right) = 0.1375\ \text{L}$$

(e) $$(0.025\ \text{L})\left(\frac{1000\ \text{mL}}{1\ \text{L}}\right) = 25\ \text{mL}$$

(f) $$342\ \text{pm}^2\left(\frac{1\times10^{-12}\ \text{m}}{1\ \text{pm}}\right)^2\left(\frac{10\ \text{dm}}{1\ \text{m}}\right)^2 = 3.42\times10^{-20}\ \text{dm}^2$$

1.2 | MOLE – BASIC INTRODUCTION

Laws of Chemical Combinations

The experimental observations of many scientists in the 18th and early 19th centuries led to the discovery of some basic laws of that governed the combinations of atoms in formation of compounds.

Law of Conservation of Mass

Antoine Lavoisier conducted several experiments on combustion to put forward this law in 1789. The law of conservation of mass states that **no detectable gain or loss of mass occurs in chemical reactions, that is, mass is conserved**. This means that if a chemical reaction takes place in a sealed vessel that permits no matter to enter or escape, the mass of the vessel and its contents after the reaction will be identical to its earlier mass. When scientists were able to make sure that *all* substances, including any gaseous reactants and/or products, were included when masses were measured, the law of conservation of mass could be truly tested.

Law of Definite Proportions

Joseph Proust worked on two samples of cupric carbonate ($CuCO_3$) – one natural and the other synthetic – and found that both the samples contained the same percentage composition of Cu (51.35%), C (38.91%) and O (9.74%). Thus, whether the samples were prepared by natural or synthetic means, the composition never altered. This discovery led him to formulate the law of definite proportions which states that **in a given chemical compound, the elements are always combined in the same proportions by mass**. It is also known as law of definite composition.

Law of Multiple Proportions

The observations made by studying other elements that form more than one compound with each other form the basis of the law of multiple proportions given by Dalton in 1803 which states that: **Whenever two elements form more than one compound, the different masses of one element that combine with the same mass of the other element are in the ratio of small whole numbers**.

Suppose a molecule of sulphur trioxide contains one sulphur and three oxygen atoms, and a molecule of sulphur dioxide contains one sulphur and two oxygen atoms. If we had just one molecule of each, then our samples each would have one sulphur atom and, therefore, the same mass of sulphur. Now, on comparing the oxygen atoms, we find that they are in a numerical ratio of 3:2. However, because all the oxygen atoms have the same mass, the mass ratio must also be 3:2.

Gay–Lussac's Law of Gaseous Volumes

J. L. Gay–Lussac (1778–1850) was a French chemist who studied the volume relationships of reacting gases. His results, published in 1809, were summarized in a statement known as Gay–Lussac's law of gaseous volumes, which states that: **When measured at the same temperature and pressure, the ratios of the volumes of reacting gases are small whole numbers**.

Thus, H_2 and O_2 combine to form water vapor in a volume ratio of 2:1. Similarly, H_2 and Cl_2 react to form HCl in a volume ratio of 1:1; and H_2 and N_2 react to form NH_3 in a volume ratio of 3:1.

$$\underset{\text{2 volume}}{\text{Hydrogen}} + \underset{\text{1 volume}}{\text{Oxygen}} \longrightarrow \underset{\text{2 volumes}}{\text{Water}}$$

$$2H_2(g) + O_2(g) \rightarrow H_2O(g)$$

Note: Gay–Lussac's law of combing volumes of gases can be considered as law of definite proportions by volume. The only difference with the law of definite proportions discussed earlier is that this law is with respect to volume, while the earlier one was with respect to mass.

Avogadro's Law

Two years later, in 1811, Amedeo Avogadro (1776–1856) used Gay–Lussac's law of combining volumes of gases to make a simple but significant generalization concerning gases known as Avogadro's law, which states that: **Equal volumes of different gases at the same temperature and pressure contain the same number of molecules**. This law was a real breakthrough in understanding the nature of gases.

1. It offered a rational explanation of Gay–Lussac's law of combining volumes of gases and indicated the **diatomic nature** of such elemental gases as hydrogen, chlorine and oxygen.
2. It provided a method for determining the molar masses of gases and for comparing the densities of gases of known molar mass.
3. It afforded a firm foundation for the development of the kinetic molecular theory.

Solved Example 1-25

The element molybdenum (Mo) combines with sulphur (S) to form a compound commonly called molybdenum disulphide which used in specialized lithium batteries. A sample of this compound contains 1.50 g of Mo for each 1.00 g of S. If a different sample of the compound contains 2.50 g of S, how many grams of Mo does it contain?

Solution

The first sample has a Mo to S mass ratio of 1.50 g of Mo/1.00 g of S. In the second sample, we know the mass of S (2.50 g) and the mass of Mo is unknown. The mass ratio of Mo to S in the second sample is, therefore,

$$\frac{\text{Mass of Mo}}{\text{2.50 g of S}}$$

Now we equate them, because the two ratios must be equal according to law of definite proportions.

$$\frac{\text{Mass of Mo}}{2.50 \text{ g of S}} = \frac{1.50 \text{ g of Mo}}{1.00 \text{ g of S}}$$

Solving for the mass of Mo gives

$$\text{Mass of Mo} = 2.50 \text{ g of S} \times \frac{1.50 \text{ g of Mo}}{1.00 \text{ g of S}} = 3.75 \text{ g of Mo}$$

Solved Example 1-26

1.80 g of a certain metal burnt in oxygen gave 3.0 g of its oxide. 1.50 g of the same metal heated in steam gave 2.50 g of its oxide. Which law is shown by this data?

Solution

In the first sample of oxide, we have weight of metal = 1.80 g and weight of oxygen = (3.0 – 1.80) g = 1.2 g. Therefore,

$$\frac{\text{Weight of metal}}{\text{Weight of oxygen}} = \frac{1.80 \text{ g}}{1.2 \text{ g}} = 1.5$$

In the second sample of the oxide, weight of metal = 1.50 g and weight of oxygen = (2.50 – 1.50) g = 1.2 g. Therefore,

$$\frac{\text{Weight of metal}}{\text{Weight of oxygen}} = \frac{1.50 \text{ g}}{1.0 \text{ g}} = 1.5$$

Thus, in both samples of the oxide the proportions of the weights of the metal and oxygen a fixed. Hence the results the law of constant proportion.

Solved Example 1-27

Phosphorus trichloride contains 22.57% of phosphorus, phosphine (PH_3) contains 91.18% of phosphorus, while hydrogen chloride gas contains 97.23% of chlorine. Prove by calculations, which law is illustrated by these data.

Solution

1 g of phosphorus will combine with hydrogen $= \frac{91.18}{8.82} = 10.33$ g

1 g of phosphorus will combine with chlorine $= \frac{77.43}{22.57} = 3.43$ g

Ratio of masses of hydrogen and chlorine that will combine with fixed mass of phosphorus will be $= \frac{10.33}{3.43} = \frac{3}{1} = 3:1$

Since hydrogen chloride gas contains 97.23% of chlorine therefore the ratio of hydrogen and chlorine in hydrogen chloride will be $= \frac{97.23}{2.77} = \frac{36}{1} = 36:1$

Thus the ratios 3:1 and 36:1 are simple multiple of each other. Therefore, the above data illustrates the law of reciprocal proportion.

Atomic and Molecular Masses

To further our discussion on atoms and molecules defined at the beginning of the chapter, we discuss the atomic and molecular masses in this section.

Atomic Mass

Atoms are so small that a slice of copper metal just big enough to detect on a good analytical balance contains about 1×10^{17} atoms. As a result, it is impossible to measure the absolute mass of a single atom. We can, however, measure the **relative** masses of different atoms through experimental means. Nowadays, these relative masses can be calculated with an apparatus known as a mass spectrometer.

For the relative mass of an atom, we need a standard with which our measurement can be compared. In earlier times, the standard used was hydrogen as it is the lightest element and it was assigned mass 1. However, in the present system of atomic masses, the standard used to calibrate these measurements is the carbon-12 (12C), which is an isotope of carbon. The unit in which atomic mass measurements are reported is the atomic mass unit (amu). By definition, the mass of a single atom of the 12C isotope is exactly 12 atomic mass units, or 12 amu. Nowadays, amu has been replaced by u which stands for unified mass.

Note: One atomic mass unit is equal to 1/12th of the mass of one ^{12}C atom.

The atomic mass of an element can be determined using any of the following methods.

1. **Dulong and Petit's law:** According to this law, the product of atomic mass and specific heat of a solid element, known as atomic heat, is approximately equal to 6.4. The atomic mass can be obtained using the relation

$$\text{Atomic mass (approx.)} = \frac{6.4}{\text{Specific heat}} \tag{1.4}$$

where specific heat is in cal g^{-1}. The exact atomic mass is calculated by first determining the equivalent mass experimentally, then dividing the approximate atomic mass with this to obtain the number closest to the valence. The exact atomic mass is obtained by multiplying equivalent mass with valence.

2. **Cannizaro method:** The atomic mass is determined as the smallest mass of the element present in any one of its compounds. It is calculated for an element by determining the molecular mass of a number of compounds containing that element, and then determining mass of the element in each compound.

3. **Vapor density of a chloride:** The vapor density and the equivalent mass of the chloride of the element is first determined experimentally. Then if valence of the element is n, the formula of the chloride is MCl_n. Then,

$$\text{Molecular mass} = \text{Atomic mass of M} + 35.5n = \text{Equivalent mass} \times n + 35.5n$$

Since molecular mass is twice the vapor density, we can obtain the valence and hence the atomic mass from the experimentally determined values of vapor density and equivalent mass.

4. **Law of isomorphism:** Compounds which form crystals of the same size and shape and can grow in saturated solutions of each other to form mixed crystals are said to isomorphous. For example, potassium sulphate and potassium chromate; zinc sulphate and iron sulphate are isomorphous. According to law of isomorphism compounds, the masses of two elements that combine with the same mass of the other elements in their respective compounds are in the ratio of their atomic masses. Also, the valence of the elements forming these compounds is the same.

Average Atomic Mass

Most elements exist in nature as mixtures of isotopes. As we have seen, the graphite in a lead pencil is composed of a mixture of ^{12}C (98.892%, 12.000 u), ^{13}C (1.108%, 13.003 u), and an infinitesimally small amount of ^{14}C (2×10^{-10}%, 14.00317 u). It is, therefore, useful to calculate the average mass of a sample of carbon atoms. Since there is a large difference in the natural abundance of these isotopes, the average mass of a carbon atom must be a weighted average of the masses of the different isotopes. Because the amount of ^{14}C is so small, the average mass of a carbon atom is calculated using only the two most abundant isotopes of the element.

$$\left(12.000\text{ u} \times \frac{98.892}{100}\right) + \left(13.003\text{ u} \times \frac{1.108}{100}\right) = 12.011\text{ u}$$

The average mass of a carbon atom is much closer to the mass of a ^{12}C atom than a ^{13}C atom because the vast majority of the atoms in a sample of carbon are ^{12}C. This weighted average of all the naturally occurring isotopes of an atom is known as the **atomic weight** of the element. It is this value that is reported beneath the symbol of the element in the periodic table. It is important to recognize that the atomic weight of carbon is 12.011 u even though no individual carbon atom actually has a mass of 12.011 u.

Molecular Mass

The **molecular mass** is defined as *the sum of the atomic masses of the elements in the molecule*. The molecular mass of water (H_2O) is 18.02 u, which is determined from the atomic weights of hydrogen and oxygen.

$$\overset{2H}{2 \times 1.01\text{ u}} + \overset{O}{16.00\text{ u}} = \overset{H_2O}{18.02\text{ u}}$$

Formula Mass

The **formula mass** is *the sum of the atomic masses of the elements in the formula*. Sodium chloride (NaCl) has a formula mass of 58.44 u, which is determined by adding the atomic weights of sodium and chlorine.

$$\overset{Na^+}{22.99\text{ u}} + \overset{Cl^-}{35.45\text{ u}} = \overset{NaCl}{58.44\text{ u}}$$

In this calculation, the atomic weights of Na and Cl were used, even though NaCl is composed of Na^+ and Cl^- ions. Compared to the mass of the protons and neutrons that make up the nucleus of Na and Cl atoms, electron mass is negligible, so losing or gaining electrons to form ions has no effect on atomic weight – Na and Na^+ have the same atomic weight, as do Cl and Cl^-. The mass calculated is called formula mass instead of molecular mass because in solid state these compounds do not exist as single entities.

For more complex ionic compounds, calculating formula mass works the same way. The formula mass of copper(II) nitrate, $Cu(NO_3)_2$, is 187.54 u.

$$\overset{Cu^{2+}}{63.55\text{ u}} + \overset{2NO_3^-}{\overset{2N}{2 \times 14.01\text{ u}} + \overset{6O}{6 \times 15.995\text{ u}}} = \overset{Cu(NO_3)_2}{187.54\text{ u}}$$

The mass in grams of one mole of an ionic compound (its molar mass) is numerically equivalent to its formula mass (in u). For example, $Cu(NO_3)_2$ has a formula mass of 187.54 u, so its molar mass is 187.54 g mol^{-1}. This relationship allows conversions to be carried out easily.

Solved Example 1-28

Naturally occurring boron is composed of 19.8% of ^{10}B and 80.2% of ^{11}B. Atoms of ^{10}B have a mass of 10.0129 u and those of ^{11}B have a mass of 11.0093 u. Calculate the average atomic mass of boron.

Solution

Average atomic mass = (0.198 × 10.0129 u) + (0.802 × 11.0093 u) = 10.8 u

Solved Example 1-29

Given that vapor densities of three substance referred to hydrogen as unity were 45, 70 and 25, respectively, and mass percent of a metal M contained in each were 22.22%, 42.86% and 40%, respectively. Calculate the atomic mass of the metal M.

Solution

From the given data, we have

Vapor densities	45	70	25
Molecular weights (u)	90	140	50
Percent by weight	22.22	42.86	40
Weight of metal M (u)	$\frac{22.22}{100} \times 90$ $= 19.99$	$\frac{42.86}{100} \times 140$ $= 60.00$	$\frac{40}{100} \times 50$ $= 20.00$

The minimum weight of metal M in various compounds is 20. Hence atomic weight = 20 u.

Solved Example 1-30

Calculate the molecular mass of CH_4.

Solution

The molecular mass of methane, CH_4

$$\begin{aligned} M_{CH_4} &= (1\times \text{Atomic mass of carbon}) \\ &\quad + (4\times \text{Atomic mass of hydrogen}) \\ &= [1(12.011\text{ u}) + 4(1.008\text{ u})] \\ &= 12.011\text{ u} + 4.032\text{ u} = 16.043\text{ u} \end{aligned}$$

Solved Example 1-31

(a) What is the molecular weight of chloroform ($CHCl_3$)?

(b) What is the mass of 2.50 mol of chloroform?

Solution

(a) For $CHCl_3$, we have

C	H	3Cl	$CHCl_3$
12.01	1.01	3×35.45	119.37 u

(b) For 1 mol, the molecular mass of chloroform is 119.37 g, so for 2.5 mol, the molecular mass would be

$$2.5\times \frac{119.37}{1} = 298\text{ g}$$

Solved Example 1-32

(a) What is the formula mass of the food preservative sodium sulphite (Na_2SO_3)?

(b) What is the mass of 1.50 mol of Na_2SO_3?

Solution

(a) The formula mass of Na_2SO_3 can be calculated as

$$\begin{aligned} &2\times \text{Atomic mass of Na} + \text{Atomic mass of S} + 3\times \\ &(\text{Atomic mass of O}) = 2\times 22.99\text{ u} + 32.07\text{ u} + 3\times (16) \\ &\qquad = 126.05\text{ amu} \end{aligned}$$

(b) Therefore, the molar mass of Na_2SO is 126 g mol^{-1}. Now, a sample containing 1.50 mol of Na has mass

$$1.50\text{ mol } Na_2SO_3 \times \frac{126.05\text{ g } Na_2SO_3}{1\text{ mol of } Na_2SO_3} = 189\text{ g } Na_2SO_3$$

Mole Concept and Molar Masses

Chemists face problems identifying the amount of a substance in terms of number of atoms present in it. This is because it takes an enormous number of atoms to give a sample large enough to be seen with the naked eye. Chemists, therefore, created a unit known as the **mole** (from Latin, meaning "a huge pile") that can serve as the bridge between chemistry on the macroscopic and atomic scales. The mole is defined as follows: **Any substance that contains the same number of particles as the number of atoms in exactly 12 g of the ^{12}C isotope of carbon**. It is the S.I. unit for the amount of substance.

A single ^{12}C atom has a mass of exactly 12 u and a mole of ^{12}C atoms has a mass of exactly 12 g.

$$1\ ^{12}\text{C atom} = 12.000\ldots\text{u}$$
$$1\text{ mol of }^{12}\text{C atoms} = 12.000\ldots\text{g}$$

As noted in the previous section, the average mass of naturally occurring carbon atoms is 12.011 u. Thus, one mole of carbon atoms would have a mass of 12.011 grams.

The mole is the most fundamental unit of chemistry because it allows us to determine the number of elementary particles in a sample of a pure substance by simply determining the mass of the sample. Assume, for example, that we want a sample of aluminium metal that contains the same number of atoms as a mole of carbon atoms. We can start by looking up the atomic weight of aluminium in the periodic table.

$$1 \text{ Al atom} = 26.982 \text{ u}$$

The atomic weight of this element is known to five significant figures. When the atomic weight is used in a calculation, however, one only needs to retain the number of digits that corresponds to the appropriate number of significant figures. The atomic weight of aluminium is a little more than twice that of a ^{12}C atom. As a result, aluminium atoms are a little more than twice as heavy as a ^{12}C atom.

$$\frac{1 \text{ Al atom}}{1\ ^{12}\text{C atom}} = \frac{26.982 \text{ u}}{12 \text{ u}} = 2.2485 \tag{1.5}$$

(The ratio of the mass of an aluminium atom to a ^{12}C atom in this calculation can be given to five significant figures because the mass of ^{12}C is based on a definition, not a measurement.)

Equation (1.5) means that if a mole of aluminium contains exactly the same number of atoms as a mole of ^{12}C, then a mole of aluminium must have a mass that is 2.2485 times the mass of a mole of ^{12}C atoms.

$$\frac{1 \text{ mol Al}}{1 \text{ mol } ^{12}\text{C}} = \frac{26.982 \text{ g}}{12 \text{ g}} = 2.2485$$

Thus, the mass of a mole of aluminium is 26.982 g.

Note: The concept of the mole serves as a bridge between the atomic and macroscopic worlds.

We can further relate mole to atomic weights and molar mass as follows: **A mole of atoms of any element has a mass in grams equal to the atomic weight of the element. The mass of a mole of a substance is often called the molar mass**.

For many years, chemists used the concept of a mole without knowing exactly how many particles there were in a mole of elemental carbon or aluminium metal. What matters is the fact that there are the same number of particles in a mole of each of these elements.

The only way to determine the number of particles in a mole is to measure the same quantity on both the atomic and the macroscopic scales. To determine this number of particles precisely, the mass of one ^{12}C atom was measured using a mass spectrometer and was found to be 1.992648×10^{-23} g.

Now, we know that

$$1 \text{ mol of } ^{12}\text{C} = 12 \text{ g}$$

Therefore, the number of atoms present in 1 mol of ^{12}C is

$$\frac{12 \text{ g}}{1 \text{ mol of } ^{12}\text{C}} \div \frac{1.992648 \times 10^{-23} \text{ g}}{1\ ^{12}\text{C atom}}$$

$$\frac{12 \text{ g}}{1 \text{ mol of } ^{12}\text{C}} \times \frac{1\ ^{12}\text{C atom}}{1.992648 \times 10^{-23} \text{ g}} = 6.023 \times 10^{23} \text{ atoms mol}^{-1}$$

The number of particles in a mole is known as **Avogadro's constant** (previously known as Avogadro's number).

In 1910 Robert Millikan measured the charge in coulombs on a single electron: 1.602×10^{-19} C. Because the charge on a mole of electrons, 96,485 C, was already known, it was possible to estimate the number of electrons in a mole for the first time. Using more recent data, we get the following results.

$$\frac{96,485 \text{ C}}{1 \text{ mol}} \times \frac{1 \text{ electron}}{1.602 \times 10^{-19}} = 6.023 \times 10^{23} \frac{\text{electrons}}{\text{mol}}$$

In everyday life units such as dozen (12) and gross (144) are used to describe a collection of items. The mole is sometimes referred to as the "chemist's dozen". The concept of the mole can be applied to any particle. We can talk about a mole of Mg atoms, a mole of Na^+ ions, a mole of electrons, or a mole of glucose molecules ($C_6H_{12}O_6$). Each time we use the term, we refer to Avogadro's number of items.

1 mol of Mg atoms contains 6.023×10^{23} atoms of Mg.
1 mol of Na^+ ions contains 6.023×10^{23} ions of Na^+.
1 mol of electrons contains 6.023×10^{23} electrons.
1 mol of photons contains 6.023×10^{23} photons.
1 mole of $C_6H_{12}O_6$ molecules contains 6.023×10^{23} $C_6H_{12}O_6$ molecules.

Once we know the number of elementary particles in a mole, we can determine the number of particles in a sample of a pure substance by weighing the sample. In general, you need two pieces of information to do calculations of this nature. You need to know the mass of a mole of the substance and the number of particles in a mole.

$$\underset{\text{(Macroscopic scale)}}{\text{Mass}} \xleftrightarrow{\text{Molar mass}} \text{Moles} \xleftrightarrow{\text{Avogadro's constant}} \underset{\text{(Atomic scale)}}{\text{Atoms}} \qquad (1.6)$$

Before we can apply the concept of the mole to compounds such as carbon dioxide (CO_2) or the sugar known as glucose ($C_6H_{12}O_6$), we have to be able to calculate the **molecular weight** of these compounds. As might be expected, the molecular weight of a compound is the sum of the atomic weights of the atoms in the formula of the compound. The average mass of a *single molecule of carbon dioxide* is the sum of the atomic weights of the three atoms in a CO_2 molecule.

Average mass of a CO_2 molecule:

$$\begin{array}{r} 1\text{ C atom} = 1(12.011\text{ u}) = 12.011\text{ u} \\ 2\text{ O atoms} = 2(15.999\text{ u}) = 31.998\text{ u} \\ \hline = 44.009\text{ u} \end{array}$$

The mass of a *mole of carbon dioxide* therefore would be 44.009 g. The average mass of a molecule of glucose is the sum of the atomic weights of the 24 atoms in a $C_6H_{12}O_6$ molecule.

Average mass of a $C_6H_{12}O_6$ molecule:

$$\begin{array}{r} 6\text{ C atoms} = 6(12.011\text{ u}) = 72.066\text{ u} \\ 12\text{ H atoms} = 12(1.0079\text{ u}) = 12.095\text{ u} \\ 6\text{ O atoms} = 6(15.999\text{ u}) = 95.994\text{ u} \\ \hline = 180.155\text{ u} \end{array}$$

The molecular weight of the compound is therefore 180.155 grams mol^{-1}.

This term is molecular weight is however, somewhat misleading for several reasons. First, no $C_6H_{12}O_6$ molecule ever has a mass equal to 180.155 u. This is the *average mass* of the sugar molecules, which contain ^{12}C and ^{13}C atoms as well as a mixture of hydrogen and oxygen isotopes. Second, some compounds do not exist as molecules, so it is misleading to talk about their "molecular" weight. Some chemists, therefore, recommend that we describe the results of these calculations as the **mass of a mole** or the ***molar mass*** of a compound. Because the term *molecular weight* has been so extensively used by chemists and is widely found in the chemical literature, we will use the terms *molar mass* and *molecular weight* interchangeably.

The diagram we used to summarize mass–mole conversions for elements can be used for chemical compounds. In this case, however, we can take the calculation one step further by using the formula of the compound to calculate the number of atoms of a given element in the sample.

$$\underset{\text{(Macroscopic scale)}}{\text{Mass}} \xleftrightarrow{\text{Molar mass}} \text{Moles} \xleftrightarrow{\text{Avogadro's constant}} \text{Molecules} \xleftrightarrow{\text{Chemical formula}} \underset{\text{(Atomic scale)}}{\text{Atoms}} \qquad (1.7)$$

Solved Example 1-33

(a) Marbles of diameter 10 mm are to be put in a square area of side 40 mm so that their centers are within this area. Find the maximum number of marbles per unit area and deduce an expression for calculating it.

(b) In a solution of 100 mL 0.05 M acetic acid, one g of active charcoal is added, which absorbs acetic acid. It is found that the concentration of acetic acid becomes 0.049 M. if surface area of charcoal is $3.01 \times 10^2 \, m^2$, calculate the area occupied by single acetic acid molecule on surface of charcoal.

(IIT-JEE 2003)

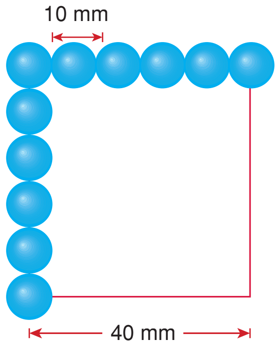


Figure 1.8

Solution

(a) Given that side of the square = 40 mm and diameter of marbles = 10 mm. The number of marbles along an edge of the square with their centers within the square = 5 (Fig. 1.8).

The number of moles of acetic acid adsorbed on the surface of charcoal = 0.001 (0.05 – 0.049)

The number of molecules of acetic acid adsorbed on the surface of charcoal = $0.001 \times 6.02 \times 10^{23} = 6.02 \times 10^{20}$

Maximum no. of marbles per unit area = 5 × 5 = 25.

(b) The number of moles of acetic acid in 100 mL (before adding charcoal) = 0.05

The number of moles of acetic acid in 100 mL (after adding charcoal) = 0.049

Given that the surface area of charcoal = $3.01 \times 10^2 \, m^2$. Hence, the area occupied by single acetic acid molecule on the surface of charcoal is

$$\frac{3 \times 10^2}{6.02 \times 10^{20}} = 5 \times 10^{-19} \, m^2$$

Solved Example 1-34

Describe the difference between the mass of a mole of oxygen atoms (O) and the mass of a mole of oxygen molecules (O_2).

Solution

Because the atomic weight of oxygen is 15.999 u, a mole of oxygen atoms has a mass of 15.999 g. Each O_2 molecule has two atoms, however, so the molecular weight of O_2 molecules is twice as large as the atomic weight of the atom.

$$1 \text{ mol of O} = 15.999 \text{ g}$$
$$1 \text{ mol of } O_2 = 31.998 \text{ g}$$

Solved Example 1-35

How many carbon atoms are there in one molecule of acetylene, C_2H_2? How many moles of carbon atoms are in one mole of C_2H_2? How many carbon atoms are in one mole of C_2H_2?

Solution

There are two atoms of carbon in one molecule of C_2H_2; two moles of carbon atoms in one mole of C_2H_2; and 1.20×10^{24} atoms of carbon in one mole of C_2H_2.

Solved Example 1-36

Set the following in increasing order of number of moles: **(a)** 4.55×10^{22} atoms of Pb, **(b)** 8.50 g of C, **(c)** 7.14×10^{22} atoms of Zn, **(d)** 0.280 mol of Ca

Solution

Converting all the quantities into mole, we get

(a) Number of moles of Pb $= \dfrac{4.55\times 10^{22}}{6.023\times 10^{23}} = 0.0755$ mol

(b) Number of moles of C $= \dfrac{8.50}{12.0} = 0.708$ mol

(c) Number of moles of Zn $= \dfrac{7.14\times 10^{22}}{6.023\times 10^{23}} = 0.118$ mol

(d) Number of moles of Ca = 0.280 mol.

Therefore, the increasing order is (a) < (c) < (d) < (b).

Mole Concept and Number of Atoms/Ions/Molecules

We know that 1 mol consists of N_A or Avogadro number of atoms/ions/molecules.

Therefore, N_A atoms/ions/molecules = 1 mol

$$1 \text{ atom/ion/molecules} = \frac{1}{N_A} \text{ mol}$$

$$\text{If we have } x \text{ atoms/ions/molecules} = \frac{x}{N_A} \text{ mol}$$

$$\text{Therefore,} \quad \text{Number of moles} = \frac{\text{Number of atoms/ions/molecules}}{N_A}$$

Solved Example 1-37

Find the number of moles in the following:

(a) 2 atoms of H

(b) 3 ions of N^{3-}

(c) 4 molecules of CO_2

Solution

(a) $\text{Number of moles} = \dfrac{\text{Number of atoms of H}}{N_A} = \dfrac{2}{N_A}$

(b) $\text{Number of moles} = \dfrac{\text{Number of ions of } N^{3-}}{N_A} = \dfrac{3}{N_A}$

(c) $\text{Number of moles} = \dfrac{\text{Number of atoms of } CO_2}{N_A} = \dfrac{4}{N_A}$

Mole Concept and Volume (L) of Ideal Gas at NTP/STP

NTP is normal temperature (25°C or 298 K) and pressure (1 atm) while STP is standard temperature (0°C or 273 K) and pressure (1 atm).

For all the ideal gases (we will cover this in Chapter 3), the ideal gas equation is followed

$$pV = nRT$$

where p is the pressure exerted by the gas in atm, V is the volume occupied by gas in L, n is the number of moles of the gas, R is the universal gas constant and T is the temperature of the gas in kelvin.

For any gas at STP

$$(1\text{ atm})V = n(0.0821 \text{ L atm K}^{-1}\text{ mol}^{-1})(0 + 273\text{ K})$$

$$n = \frac{V}{22.4}$$

For any gas at NTP

$$(1\ \text{atm})V = n(0.0821\ \text{L atm K}^{-1}\ \text{mol}^{-1})(25 + 273\ \text{K})$$

$$n = \frac{V}{24.46}$$

But we use the general equation as

$$\text{Number of moles of an ideal gas} = \frac{\text{Volume (L) at STP/NTP}}{22.4}$$

Solved Example 1-38

Calculate the number of moles in the following cases (assuming ideal gases).

(a) 67.2 L of CO_2 at STP

(b) 2240 mL of N_2 at STP

(c) 18 mL of H_2O (density = 1 g mL^{-1})

Solution

(a) $$\text{Number of moles of } CO_2 = \frac{67.2}{22.4} = 3\ \text{mol}$$

(b) $$\text{Number of moles of } N_2 = \frac{2240}{22400} = 0.1\ \text{mol}$$

(c) $$\text{Number of moles of } H_2O = \frac{18}{22400}$$

This is wrong!

We have not mentioned STP or NTP in the above equation.

In this case,

$$18\ \text{mL of } H_2O = 18\ \text{g of } H_2O$$

Therefore,

$$\text{Number of moles} = \frac{\text{Weight of } H_2O(g)}{\text{Molecular weight of } H_2O(g)}$$

$$= \frac{18}{18} = 1\ \text{mol}$$

1.3 | PERCENTAGE COMPOSITION

It is often useful to know the **percent by mass** of the different elements in a compound. Percent by mass can be determined experimentally or from the chemical formula. When the formula of a compound is known, the first step in this calculation involves determining the molecular weight of the compound. The molecular weight of ethanol (CH_3CH_2OH), for example, would be calculated as follows.

Average mass of CH_3CH_2OH molecule:

$$\begin{aligned} 2\ \text{C atoms} &= 2(12.011\ \text{u}) = 24.022\ \text{u} \\ 6\ \text{H atoms} &= 6(1.0079\ \text{u}) = 6.0474\ \text{u} \\ 1\ \text{O atoms} &= 1(15.999\ \text{u}) = 15.999\ \text{u} \\ \hline &= 46.068\ \text{u} \end{aligned}$$

A mole of ethanol, therefore, weighs 46.068 g. The percent by mass of carbon in ethanol is, therefore, the mass of carbon in a mole of ethanol divided by the mass of a mole of ethanol, times 100.

$$\frac{24.022\ \text{g of C}}{46.068\ \text{g of } CH_3CH_2OH} \times 100 = 52.145\%\ \text{of C}$$

The percent by mass of hydrogen and oxygen in ethanol can be calculated in a similar fashion.

$$\frac{6.0474\ \text{g of H}}{46.068\ \text{g of } CH_3CH_2OH} \times 100 = 13.127\%\ \text{of H}$$

$$\frac{15.999\ \text{g of O}}{46.068\ \text{g of } CH_3CH_2OH} \times 100 = 34.729\%\ \text{of O}$$

In general, the percentage composition of an element in a compound can be calculated using the relation

$$\text{Mass \% of an element} = \frac{\text{Mass of the element in the compound}}{\text{Molar mass of the compound}} \times 100 \qquad (1.8)$$

Solved Example 1-39

A mixture of $CaCO_3$ and $MgCO_3$ weighing 1.84 g on heating left a residue weighing 0.96 g. Calculate the percentage composition of each in the mixture.

Solution

First, we determine the residue

$$CaCO_3 \longrightarrow CaO + CO_2$$
$$MgCO_3 \longrightarrow MgO + CO_2$$

CO_2 (carbon dioxide) being gas escapes, so residue include MgO and CaO. Let the sample contains x g of $CaCO_3$. Now, mass of $MgCO_3 = (1.84 - x)$ g. Thus,

$$\text{Moles of } CaCO_3 = \frac{x}{100} \text{ and Moles of } MgCO_3 = \frac{1.84 - x}{84}$$

From reaction stoichiometry, we have:

$$1 \text{ mol of } CaCO_3 \equiv 1 \text{ mol of CaO}$$

$$\frac{x}{100} \text{ mol of } CaCO_3 \equiv \frac{x}{100} \text{ mol of CaO} \equiv \frac{x}{100} \times 56 \text{ g of CaO}$$

Similarly, 1 mol of $MgCO_3 \equiv 1$ mol of MgO

$$\frac{1.84 - x}{84} \text{ mol of } MgCO_3 \equiv \frac{1.84 - x}{84} \text{ mol of MgO}$$
$$\equiv \frac{1.84 - x}{84} \times 40 \text{ g of MgO}$$

Now, the total grams of MgO and CaO (i.e., residue) = 0.96 g

$$\frac{56x}{100} + \frac{40}{84}(1.84 - x) = 0.96$$

or

$$0.56x + 0.87 - 0.47x = 0.96$$
$$0.09x = 0.09 \Rightarrow x = 1.0 \text{ g}$$

So, we have 1.0 g of $CaCO_3$ and (1.84 – 1.0) = 0.84 g of $MgCO_3$ in the sample. Hence, the percentage composition can be found out as follows:

$$\%CaCO_3 = \frac{1.0}{1.84} \times 100 = 54.34\%$$
$$\%MgCO_3 = (100 - 54.34)\% = 45.66\%$$

Empirical and Molecular Formulae

The **empirical formula**, or *simplest formula*, gives the smallest whole number ratio of atoms present in a compound. This formula gives the relative number of atoms of each element in the compound.

To calculate the empirical formula of a compound from percent composition, we follow three steps.

1. Convert percent composition into an actual mass.
2. Convert mass into moles of each element.
3. Find the whole number ratio of the moles of different elements.

Let us approach a problem using percent by mass data by examining the compound methane. Methane is 74.9% carbon and 25.1% hydrogen by mass. A 100 g sample of the gas, therefore, contains 74.9 g of carbon and 25.1 g of hydrogen.

$$100 \text{ g of methane} \times \frac{74.9 \text{ g of C}}{100 \text{ g of methane}} = 74.9 \text{ g of C}$$

$$100 \text{ g of methane} \times \frac{25.1 \text{ g of H}}{100 \text{ g of methane}} = 25.1 \text{ g of H}$$

This is useful information because we can use the molar mass of these elements to convert the grams of carbon and hydrogen in this sample into moles of each element.

$$74.9 \text{ g of C} \times \frac{1 \text{ mol of C}}{12.011 \text{ g of C}} = 6.24 \text{ mol of C}$$

$$25.1 \text{ g of H} \times \frac{1 \text{ mol of H}}{1.0079 \text{ g of H}} = 24.9 \text{ g of H}$$

We now know the number of moles of carbon atoms and the number of moles of hydrogen atoms in a sample. We also know that there is always the same number of atoms in a mole of atoms of any element. It might, therefore, be useful to look at the ratio of the moles of these elements in the sample.

$$\frac{24.9 \text{ mol of H}}{6.24 \text{ mol of C}} = 3.99$$

The 100 g sample of methane, therefore, contains about four times as many moles of hydrogen atoms as moles of carbon atoms, within experimental error. This means that there are four times as many hydrogen atoms as carbon atoms in this sample.

The above example tells us the simplest or **empirical formula** (smallest whole number ratio of atoms) of the compound, but not necessarily the **molecular formula** (actual whole number ratio of atoms in a molecule). These results are consistent with molecules that contain one carbon atom and four hydrogen atoms: CH_4. However, they are also consistent with formulas such as C_2H_8, C_3H_{12}, C_4H_{16} and so on. All we know at this point is that the molecular formula for the molecule is some multiple of the empirical formula, CH_4. Using other experimental techniques, it is possible to show that the molecular weight of methane is 16 g mol^{-1}, which is consistent with a molecular formula of CH_4.

The **molecular formula** is the true formula, representing the total number of atoms of each element present in one molecule of a compound. It is entirely possible that two or more substances will have the same percent composition yet be distinctly different compounds.

For example, both acetylene (C_2H_2) and benzene (C_6H_6) contain 92.3% C and 7.7% H. The smallest ratio of C and H corresponding to these percentages is CH (1:1). Therefore, the *empirical* formula for both acetylene and benzene is CH, even though the *molecular* formulas are C_2H_2 and C_6H_6, respectively. Often the molecular formula is the same as the empirical formula. If the molecular formula is not the same, it will be an integral (whole number) multiple of the empirical formula.

To find the molecular formula, the integral multiple can be found as

$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}} \tag{1.9}$$

Now, Molecular formula = Empirical formula × n
For example,

$$CH = \text{Empirical formula}$$
$$(CH)_2 = C_2H_2 = \text{Acetylene (molecular formula)}$$
$$(CH)_6 = C_6H_6 = \text{Benzene (molecular formula)}$$

Table 1.5 shows empirical and molecular formula relationships of other compounds.

Table 1.5 Some empirical and molecular formulae

Substance	Empirical formula	Molecular formula	Substance	Empirical formula	Molecular formula
Acetylene	CH	C_2H_2	Diborane	BH_3	B_2H_6
Benzene	CH	C_6H_6	Hydrazine	NH_2	N_2H_4
Ethylene	CH_2	C_2H_4	Hydrogen	H	H_2
Formaldehyde	CH_2O	CH_2O	Chlorine	Cl	Cl_2
Acetic acid	CH_2O	$C_2H_4O_2$	Bromine	Br	Br_2
Glucose	CH_2O	$C_6H_{12}O_6$	Oxygen	O	O_2
Hydrogen chloride	HCl	HCl	Nitrogen	N	N_2
Carbon dioxide	CO_2	CO_2	Iodine	I	I_2

Solved Example 1-40

A salt composed of titanium and oxygen is 74.96% titanium by mass. Determine the empirical formula of the titanium oxide.

Solution

100.00 g of the salt contain 74.96 g of titanium and 25.04 g oxygen. The number of moles of Ti and O can be found as

$$74.96\text{ g Ti}\times\frac{1\text{ mol Ti}}{47.9\text{ g Ti}}=1.56\text{ mol Ti}$$

$$25.04\text{ g O}\times\frac{1\text{ mol O}}{16.0\text{ g O}}=1.56\text{ mol O}$$

The simplest ratio is 1:1. So, the empirical formula is TiO.

Solved Example 1-41

Molecular formula of acetic acid is CH_3COOH. What are the number of atoms present in its empirical formula?

Solution

We have the integral multiple as

$$n=\frac{\text{Molecular mass}}{\text{Empirical formula}}$$

$\Rightarrow n=2$ (from Table 1.5)

$$\text{So, empirical formula}=\frac{\text{Molecular mass}}{2}$$

Thus, empirical formula $=\frac{CH_3COOH\text{ or }C_2H_4O_2}{2}=CH_2O$.

So, the total number of atoms present in empirical formula is 4.

Solved Example 1-42

12.78 g of an organic compound containing C, H and O and undergoes combustion to produce 25.56 g of carbon dioxide and 10.46 g of water. What is the empirical formula of the organic compound?

Solution

From the given data, we have

Element	Moles	Grams	Relative number of moles	Simplest whole ratio
C	$\frac{1\text{ mol}}{44\text{ g}}\times 25.56\text{ g}$ $=0.581\text{ mol}$	0.581×12 $=6.97\text{ g}$	$\frac{0.581}{0.291}\simeq 2$	2
H	$\frac{2\text{ mol}}{18\text{ g}}\times 10.46\text{ g}$ $=1.162\text{ mol}$	1.162×1 $=1.162\text{ g}$	$\frac{1.162}{0.291}\simeq 4$	4
O	$\frac{12.78-6.97-1.16}{16}$ $=0.291\text{ mol}$	$12.78-6.97$ -1.16 $=4.65\text{ g}$	$\frac{0.291}{0.291}\simeq 1$	1

Therefore, empirical formula $=C_2H_4O$.

Solved Example 1-43

If 30 mL of a gaseous hydrocarbon requires 90 mL of O_2 for complete combustion and 60 mL of CO_2 is formed in the process, the molecular formula of hydrocarbon will be

(a) C_2H_2 **(b)** CH_4 **(c)** C_2H_4 **(d)** C_2H_6

Solution

Let the hydrocarbon be C_xH_y, then it undergoes combustion in the following manner:

$$\begin{array}{lcccc} & C_xH_y & +\left(x+\frac{y}{4}\right)O_2 & \longrightarrow xCO_2 & +\frac{y}{2}H_2O \\ & 30\,\text{mL} & 90\,\text{mL} & 60\,\text{mL} & \\ & 1\,\text{mL} & 3\,\text{mL} & 2\,\text{mL} & \\ \text{or} & 1\,\text{mol} & 3\,\text{mol} & 2\,\text{mol} & \end{array}$$

Equal volumes of all gases contain equal number of molecules at the same conditions of temperature and pressure. Therefore, we have

$$x = 2 \text{ and } x+\frac{y}{4} = 3 \Rightarrow \frac{y}{4} = 3-2 = 1 \Rightarrow y = 4$$

Thus, the molecular formula = C_2H_4.

1.4 | MOLE CONCEPT – STOICHIOMETRY

A chemical equation describes what happens when a chemical change or reaction takes place. A chemical equation uses the chemical symbols and formulas of the reactants and products and other symbolic terms to represent a chemical reaction. Consider the reaction between hydrogen and oxygen to form water, represented by the chemical equation

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$$

The substances that appear on the left of the arrow (hydrogen and oxygen) are called **reactants**; they are the substances that are present before the reaction begins. The substances to the right of the arrow (water) are called **products**. The physical states of the reactants and products, that is whether they are solid, liquid or gases, are indicated by the letters (s), (l) or (g), respectively. A substance that is dissolved in water is indicated by writing (aq) after the formula of the compound, indicating that the substance is present as an aqueous solution.

Balancing of Chemical Equations

A **balanced equation** contains the same number of each kind of atom on each side of the equation. The balanced equation, therefore, obeys the law of conservation of mass. The way to balance an equation is to adjust the number of atoms of each element so that they are the same on each side of the equation, but a correct formula is never changed in order to balance an equation. The general procedure for balancing equations is as follows:

1. **Identify the reaction:** Write a description or word equation for the reaction. For example, let us consider mercury(II) oxide decomposing into mercury and oxygen.

$$\text{Mercury(II) oxide} \xrightarrow{\text{Heat}} \text{Mercury} + \text{Oxide}$$

2. **Write the unbalanced (skeleton) equation:** Make sure that the formula for each substance is correct and that reactants are written to the left and products to the right of the arrow. For example,

$$HgO \xrightarrow{\text{Heat}} Hg + O_2$$

   The correct formulas must be known or determined from the periodic table, lists of ions, or experimental data.

3. **Balance the equation:** Use the following process as necessary.

   (a) Count and compare the number of atoms of each element on each side of the equation and determine those that must be balanced:

   Hg is balanced (1 on each side)
   O needs to be balanced (1 on reactant side, 2 on product side)

   (b) Balance each element, one at a time, by placing whole numbers (coefficients) in front of the formulas containing the unbalanced element. Select the smallest coefficients that will give the same number of atoms of the element on each side. A coefficient placed in front of a formula multiplies every atom in the formula by that number (e.g., 2 H_2SO_4 means two units of sulphuric acid and also means four H atoms, two S atoms and eight O atoms). Place a 2 in front of HgO to balance O:

$$2HgO \xrightarrow{\text{Heat}} Hg + O_2$$

(c) Check all other elements after each individual element is balanced to see whether, in balancing one element, other elements have become unbalanced. Make adjustments as needed. Now, Hg is not balanced. To adjust this, we write a 2 in front of Hg.

$$2HgO \xrightarrow{\text{Heat}} 2Hg + O_2 \ \text{(balanced)}$$

(d) Do a final check, making sure that each element and/or polyatomic ion is balanced and that the smallest possible set of whole-number coefficients has been used:

$$2HgO \xrightarrow{\text{Heat}} 2Hg + O_2 \quad \text{(correct form)}$$
$$4HgO \xrightarrow{\text{Heat}} 4Hg + 2O_2 \ \text{(incorrect form)}$$

Note: Some tips for balancing an equation:

1. Balance elements other than H and O first.
2. Elements should be balanced.
3. Balance as a group those polyatomic ions that appear unchanged on both sides of the arrow.

Stoichiometry and Stoichiometric Calculations

In chemical processes carried out in laboratories or industry, the basic question is about the amount of reactants required to prepare a certain amount of product. The quantitative relationships among the reacting materials and the products formed are known as **stoichiometry**. The term stoichiometry comes from the Greek words – *stoicheion* (meaning element) and *metron* (meaning measurement). All the steps necessary to do calculations of this sort are grouped under the heading stoichiometry and are based on the use of balanced chemical equation for the reaction. The chemical equation gives relative amounts of molecules of each type that participate in the reaction. The coefficients 2 for H_2 and H_2O are called **stoichiometric coefficients**. In the balanced chemical equation, they represent the number of molecules (moles) of reactants and products taking part in the reaction. Thus according to the above chemical reaction, we know that

1. Two moles of H_2(g) react with one mole of O_2(g) to form two moles of H_2O(l).
2. Two molecules of H_2(g) react with one molecule of O_2(g) to form two molecules of H_2O(l).
3. 2×2 g of H_2(g) react with 32 g of O_2(g) to form 2×18 g of H_2O(l).
4. 2×22.4 L of H_2(g) react with 22.4 L of O_2(g) to form 2×22.4 L of H_2O(g).

Using these relations, we conclude that the data can be interconverted as

For a reaction Mass ↔ Moles ↔ Number of molecules

$$aA + bB \rightarrow (cC + dD)$$
$$\frac{n_A}{a} = \frac{n_B}{b} = \frac{n_C}{c} = \frac{n_D}{d}$$

The three main steps in stoichiometric calculations for any chemical reaction are:

1. **Determine the number of moles of starting substance:** Find the starting material or product of the reaction for which you know both the mass of the sample and the formula of the substance. Use the molecular weight of this substance to convert the number of grams in the sample into an equivalent number of moles.
2. **Determine the mole ratio of the desired substance to the starting substance:** Use the balanced equation for the reaction to create a mole ratio that can convert the number of moles of the starting substance into moles of the desired substance.
3. **Calculate the desired substance in the units specified in the problem:** Use the molecular weight of the desired substance of the reaction to convert the number of moles involved in the reaction into grams or the units specified.

All calculations that start with the mass of one substance (A) and require the mass of a second substance (B) as the answer can be determined using the sequence of steps shown in Fig. 1.9.

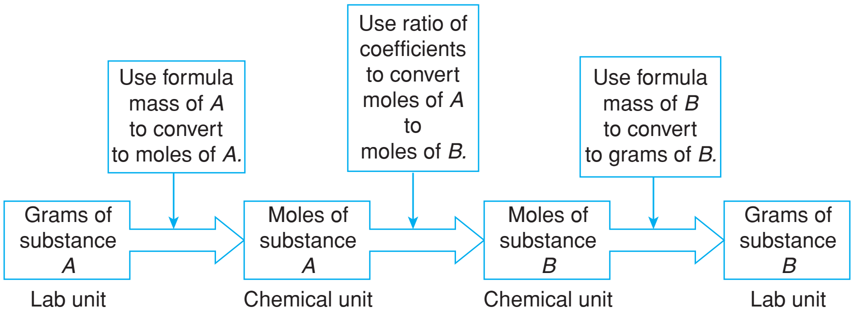

Use formula mass of *A* to convert to moles of *A*.
Use ratio of coefficients to convert moles of *A* to moles of *B*.
Use formula mass of *B* to convert to grams of *B*.
Grams of substance *A*
Moles of substance *A*
Moles of substance *B*
Grams of substance *B*
Lab unit
Chemical unit
Chemical unit
Lab unit

Figure 1.9 The sequence of calculations for solving stoichiometry problems.

Solved Example 1-44

Calculate the amount of calcium of oxide required when it reacts with 852 g of P_4O_{10}. **(IIT-JEE 2005)**

Solution

The required reaction is: $6CaO + P_4O_{10} \rightarrow 2Ca_3(PO_4)_2$

Moles of $P_4O_{10} = 852/284 = 3$ and that of $CaO = 3 \times 6 = 18$.

According to the reaction, we have

1 mol of P_4O_{10} reacts with 6 mol of CaO

So, 3 mol of P_4O_{10} reacts with $(3 \times 6) = 18$ mol of CaO.

Thus, the amount of calcium of oxide required = 18 × 56 = 1008 g.

Solved Example 1-45

Silver nitrate, $AgNO_3$, reacts with iron(III) chloride, $FeCl_3$, to give silver chloride, AgCl, and iron(III) nitrate, $Fe(NO_3)_3$. A solution containing 18.0 g of $AgNO_3$ was mixed with a solution containing 32.4 g of $FeCl_3$. How many grams of which reactant remain after the reaction is over?

Solution

The reaction taking place is:

$$3AgNO_3 + FeCl_3 \rightarrow 3AgCl + Fe(NO_3)_3$$

The amount of $FeCl_3$ that is required to react completely with all of the available silver nitrate (18.0 g) is

$$\left(\frac{1\text{ mol AgNO}_3}{169.87\text{ g AgNO}_3}\right)\left(\frac{1\text{ mol FeCl}_3}{3\text{ mol AgNO}_3}\right)\left(\frac{162.21\text{ g FeCl}_3}{1\text{ mol FeCl}_3}\right)$$

$= 5.73\text{ g FeCl}_3$

Since more than this minimum amount is available, $FeCl_3$ is present in excess, and $AgNO_3$ must be the limiting reactant.

We know that only 5.73g $FeCl_3$ will be used. Therefore, the amount left unused is:

$$32.4\text{ g total} - 5.73\text{ g used} = 26.7\text{ g FeCl}_3$$

Solved Example 1-46

A compound that is 31.9% K and 28.9% Cl and rest oxygen by mass decomposes when heated to give O_2 and a compound that is 52.4% K and 47.6% Cl by mass. Write a balanced chemical equation for the reaction.

Solution

The empirical formula of the reactant compound:

$$31.9\text{ g of K} \times \frac{1\text{ mol of K}}{39.098\text{ g of K}} = 0.816\text{ mol of K} \qquad (1)$$

$$28.9\text{ g of Cl} \times \frac{1\text{ mol of Cl}}{35.453\text{ g of Cl}} = 0.815\text{ mol of Cl} \qquad (2)$$

$$39.2\text{ g of O} \times \frac{1\text{ mol of O}}{15.999\text{ g of O}} = 2.45\text{ mol of O} \qquad (3)$$

Dividing the RHS of Eqs. (1)–(3) by smallest value 0.815, we get

$$\frac{0.816}{0.815} = 1\text{ mol of K} \qquad \frac{0.815}{0.815} = 1\text{ mol of Cl}$$

$$\frac{2.45}{0.815} = 3\text{ mol of O}$$

The empirical formula of the reactant compound is $KClO_3$. The empirical formula of the product compound is:

$$52.4 \text{ g of K} \times \frac{1 \text{ mol of K}}{39.098 \text{ g}} = 1.34 \text{ mol of K}$$

$$47.6 \text{ g of Cl} \times \frac{1 \text{ mol of Cl}}{35.453 \text{ g}} = 1.34 \text{ mol of Cl}$$

Therefore, the product compound is KCl, and the balanced equation for the decomposition is

$$2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g)$$

Solved Example 1-47

Consider the following reaction:

$$CO(g) + 2H_2(g) \rightarrow CH_3OH(g)$$

(a) How many moles of H_2 are required to react completely with 2 mol of CO?

(b) How many H_2 molecules would be needed to consume 2 mol of CO? How many H atoms would be needed?

(c) How many grams of H_2 are required to consume 2 mol of CO?

Solution

(a) $2 \times 2 = 4$ mol of H_2 are needed to consume 2 mol of CO.

(b) $4 \times 6.023 \times 10^{23} = 2.41 \times 10^{24}$ molecules would be needed to consume 2 mol of CO; and $2 \times 2.41 \times 10^{24} = 4.82 \times 10^{24}$ atoms will be needed to consume 2 mol of CO.

(c) The molar mass of H_2 is 2.0 g mol^{-1}. Four moles of H_2 will have a mass of $4 \times 2 = 8$ g.

Limiting Reagent

In the case of a chemical reaction, *if* specific amounts of each reactant are mixed, the reactant that produces the least amount of product is called the **limiting reagent**. In other words, the amount of product formed is limited by the reactant that is completely consumed. We can illustrate this with the simple example of the production of water from its elements, hydrogen and oxygen.

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$$

The stoichiometry of the reaction tells us that two moles (4.0 g) of hydrogen react with one mole (32.0 g) of oxygen to produce two moles (36.0 g) of water. Thus, any time hydrogen and oxygen react in a 4:32 mass ratio, all reactants are consumed and only product appears. *When reactants are mixed in exactly the mass ratio determined from the balanced equation, the mixture is said to be stoichiometric*.

$$4.0 \text{ g } H_2 + 32.0 \text{ g } O_2 \rightarrow 36.0 \text{ g } H_2O \text{ (stoichiometric)}$$

What if we mix a 6.0 g quantity of H_2 with a 32.0 g quantity of O_2? Do we produce 38.0 g water? No, we still produce only 36.0 g of H_2O using only 4.0 g of the H_2. Thus, H_2 is present in excess, and the amount of product is limited by the amount of O_2 present. In this case, O_2 becomes the limiting reactant.

$$6.0 \text{ g } H_2 + \underset{\text{(Limiting reactant)}}{32.0 \text{ g } O_2} \rightarrow 36.0 \text{ g } H_2O + \underset{\text{(In excess)}}{2.0 \text{ g } H_2}$$

If we mix a 4.0 g quantity of H_2 with a 36.0 g quantity of O_2, 36.0 g of H_2O is again produced. In this case, the H_2 is completely consumed and limits the amount of water formed. Thus, H_2 is now the limiting reactant and O_2 is present in excess.

$$\underset{\text{(Limiting reactant)}}{4.0 \text{ g } H_2} + 36.0 \text{ g } O_2 \rightarrow 36.0 \text{ g } H_2O + \underset{\text{(In excess)}}{4.0 \text{ g } O_2}$$

Note: The following sequence of steps is helpful in working limiting reagent problems.

1. Calculate the amount of product (moles or grams, as needed) formed from each reactant.
2. Determine which reactant is limiting. (The reactant that gives the least amount of product is the limiting reactant; the other reactant is in excess.)
3. Once we have identified the limiting reactant, the amount of product formed can be determined. It is the amount determined by the limiting reactant.
4. If we need to know how much of the other reactant remains, we calculate the amount of the other reactant required to react with the limiting reactant, and then subtract this amount from the starting quantity of the reactant. This gives the amount of that substance that remains unreacted.

Solved Example 1-48

Assume that 4 g of $I_2(s)$ are allowed to react with 4 g of Mg(s) according to the following chemical equation.

$$Mg(s) + I_2(s) \rightarrow MgI_2(s)$$

What is the limiting reagent in this reaction?

Solution

In the balanced chemical equation I_2 and Mg react in a one-to-one mole ratio. Therefore, 4 g of I_2 equals $4/(2 \times 126) = 0.016$ mol, while 4 g of Mg equals $4/24 = 0.16$ mol. Thus, there is ten times more Mg present than I_2. Hence, I_2 is the limiting reagent.

Solved Example 1-49

How many mole of lead(II) chloride will be formed from a reaction between 6.5 g of PbO and 3.2 g of HCl?

Solution

The reaction equation is $PbO + 2HCl \rightarrow PbCl_2 + H_2O$. Molar mass of PbO = 223 g mol^{-1}. Now,

Moles of PbO $= \dfrac{6.5}{223} = 0.029$ mol and moles of HCl $= \dfrac{3.2}{36.5} = 0.088$ mol

1 mol of PbO reacts with 2 mol of HCl. Therefore, PbO is a limiting reagent.

Hence, 0.029 mol of PbO will produce $PbCl_2 = 0.029$ mol

Theoretical and Actual Yields

The quantities of the products we have been calculating from chemical equations represent the maximum yield (100%) of product according to the reaction represented by the equation. Many reactions, especially those involving organic substances, fail to give a 100% yield of product. The main reasons for this failure are the side reactions that give products other than the main product and the fact that many reactions are reversible. In addition, some product may be lost in handling and transferring from one vessel to another. The ***theoretical yield*** of a reaction is the calculated amount of product that can be obtained from a given amount of reactant, according to the chemical equation. The ***actual yield*** is the amount of product that we finally obtain. The ***percent yield*** is the ratio of the actual yield to the theoretical yield multiplied by 100. Both the theoretical and the actual yields must have the same units to obtain a percent:

$$\frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100 = \text{Percent yield}$$

Solved Example 1-50

A sample of calcium oxide whose mass was 12 g was treated with 46.0 g of water to prepare calcium hydroxide.

(a) Which compound was the limiting reactant?

(b) Calculate the theoretical yield of $Ca(OH)_2$.

Solution

(a) The reaction equation is $CaO + H_2O \rightarrow Ca(OH)_2$. From the equation, we have

$$12\text{ g of CaO} = \frac{12}{56.1} = 0.23\text{ mol}$$

$$46.0\text{ g of }H_2O = \frac{46}{18} = 2.55\text{ mol}$$

It follows that one mole of CaO reacts with one mole of H_2O. Therefore, H_2O is present in excess and some of it will remain unreacted when the reaction is over. Hence, CaO is the limiting reagent.

(b) Now, 56.1 g of CaO reacts with 18 g of water to form $Ca(OH)_2$

Then 12 g of CaO reacts with $\frac{18 \times 12}{56.1} = 3.857$ g of water

Now, 18 g of water give 74 g of $Ca(OH)_2$

So, 3.857 g will yield $= \frac{74}{18} \times 3.857 = 15.87$ g

Thus, the theoretical yield of $Ca(OH)_2$ is 15.87 g.

1.5 | PRINCIPLE OF ATOM CONSERVATION (POAC)

The principle states that moles of atoms of an element are conserved throughout the reaction (provided the reactants are converted to products completely).

Advantages of using POAC method over stoichiometry

(a) No need to balance the equation.

(b) Complete reactions are not required.

Let us understand the concept of POAC by the following solved examples.

Solved Example 1-51

Find the moles of $BaSO_4$ in the following question, provided all S is converted from reactants to products.

$$\underset{(2\text{ moles})}{S} \xrightarrow[\text{Steps}]{\text{Several}} BaSO_4$$

Solution

In the above equation, we do not know the series of equations which have occurred in the transition of S to $BaSO_4$. But as we know S is converted to $BaSO_4$, so we can apply POAC on S.

Therefore,

$$(\text{moles of S})_{\text{before}} = (\text{moles of S})_{\text{after}}$$

$$2 = 1 \times n_{BaSO_4}$$

$$n_{BaSO_4} = 2$$

Solved Example 1-52

$$\underset{(n_1\text{ moles})}{A_xB_yC_z} \rightarrow \underset{(n_2\text{ moles})}{A_2B_3} + \underset{(n_3\text{ moles})}{A_3C}$$

If A is conserved, find the relation between A, B and C.

Solution

Applying POAC on A

$$(\text{No. of moles of A})_{\text{before}} = (\text{No. of moles of A})_{\text{after}}$$

$$x \times n_1 = 2 \times n_2 + 3 \times n_3$$

Solved Example 1-53

Assuming atoms of all the elements are conserved. Find the number of moles of the unknown quantities in the reaction.

$$\underset{(1\text{ mol})}{C_6H_{12}O_6} + \underset{(n=?)}{O_2} \rightarrow \underset{(n=?)}{CO_2} + \underset{(n=?)}{H_2O}$$

Solution

If we are using POAC, we do not need to balance the equation

Applying POAC on C

$$(\text{No. of moles of C})_{\text{before}} = (\text{No. of moles of C})_{\text{after}}$$
$$6 \times n_{C_6H_{12}O_6} = 1 \times n_{CO_2}$$
$$n_{CO_2} = 6$$

Applying POAC on H

$$(\text{No. of moles of H})_{\text{before}} = (\text{No. of moles of H})_{\text{after}}$$
$$12 \times n_{C_6H_{12}O_6} = 2 \times n_{H_2O}$$
$$n_{H_2O} = 6$$

Applying POAC on O

$$(\text{No. of moles of O})_{\text{before}} = (\text{No. of moles of O})_{\text{after}}$$
$$6 \times n_{C_6H_{12}O_6} + 2 \times n_{O_2} = 2 \times n_{CO_2} + 1 \times n_{H_2O}$$
$$6 \times 1 + 2 \times n_{O_2} = 2 \times 6 + 1 \times 6$$
$$n_{O_2} = 6$$

Note: Though POAC looks easy to apply, it is one of the common areas of mistakes for most of the students. Whenever, a balanced equation is provided, always use stoichiometry to solve the problems. Only if equation is not provided or not balanced, use POAC to solve the problems.

1.6 | CONCENTRATION TERMS

The reactions are carried out in the laboratories in solutions. So it is important to understand the constitution of a solution and the different ways to express the amount of its components. Solutions contain two components: a solute and a solvent. The substance that dissolves is the **solute**. The substance in which the solute dissolves is called the **solvent**.

Note: Two general rules can be used to decide which component of a solution is the solute and which is the solvent.

1. Any reagent that undergoes a change in state when it forms a solution is the *solute*. Thus, when gaseous HCl dissolves in water to form an aqueous solution, HCl is the solute.
2. If neither component of the solution undergoes a change in state, the component present in the smallest quantity is the *solute*.

For stoichiometric calculations in laboratory and industry, we need more quantitative methods of expressing concentrations of the components. The concentration of a substance in a given volume of solution can be expressed in the following ways.

1. **Mass percent (*w*/*w*):** This quantity expresses the mass of solute per 100 g of solution. Therefore, in 100 g of a solution that is 25% by mass HCl, there are 25 g of HCl and 75 g of H_2O. The expression for percent by mass is

$$\%\text{ by mass (solute)} = \frac{\text{Mass of solute}}{\text{Mass of solute} + \text{Mass of solvent}} \times 100$$
$$= \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 100$$

2. **Volume percentage (*V*/*V*):** Solutions that are formulated from two liquids are often expressed as volume percent with respect to the solute. The volume percent is the volume of a liquid in 100 mL of solution. The label on a bottle of ordinary rubbing alcohol reads "isopropyl alcohol, 70% by volume." Such a solution could be made by mixing 70 mL of alcohol with water to make a total volume of 100 mL, but we cannot use 30 mL of water, because the two volumes are not necessarily additive:

$$\%\text{ by volume (solute)} = \frac{\text{Volume of liquid}}{\text{Volume of solution}} \times 100$$

3. **Mass by volume (*w*/*V*) percentage:** This method expresses concentration as grams of solute per 100 mL of solution. With this system, a 10.0% m/V glucose solution is made by dissolving 10.0 g of glucose in water, diluting to 100 mL and mixing. The 10.0% m/V solution could also be made by diluting 20.0 g to 200 mL, 50.0 g to 500 mL and so on. Of course, any other appropriate dilution ratio may be used:

$$\%\text{ mass by volume (solute)} = \frac{\text{Mass of solute}}{\text{Volume of solution (mL)}} \times 100$$

Note: In case of solutions, specific gravity is used instead of density. The difference between the two is as follows: Density is defined as the ratio of mass of solute to volume of solution at a specific temperature, whereas specific gravity is defined as the ratio of mass of solution to mass of an equal volume of water at a specified temperature.

In case the specified temperature is 4°C, density is equal to specific gravity as density of water at 4°C is 1 g mL^{-1}. However, in case the specified temperature is other than 4°C, then

$$\text{Density of solute} = \text{Specific gravity} \times \text{Density of water}$$

4. **Mole fraction:** It is the ratio of number of moles of the component (solute) to the total number of moles of the components of the solution (solute + solvent). Mole fraction has the same form as mass fraction except that mole, not mass, is considered.

$$\text{Mole fraction of solute} = \frac{\text{Moles of solute}}{\text{Moles of solute} + \text{Moles of solvent}}$$

If a solution is prepared by dissolving n_A moles of component A in n_B moles of component of B, then the mole fraction of A and B is given by the relation:

$$\text{Mole fraction of A } (x_A) = \frac{n_A}{n_A + n_B}$$

$$\text{Mole fraction of B } (x_B) = \frac{n_B}{n_A + n_B}$$

Note that the mole fraction is related to the masses of the components by the following expression.

$$\text{Mole fraction of A} = \frac{\dfrac{m_A}{M_A}}{\dfrac{m_A}{M_A} + \dfrac{m_B}{M_B}}$$

where m is the mass of solute/solvent taken and M_B is its molar mass.

5. **Molarity:** The molarity of a solution is defined as the number of moles of solute per liter of solution. Molarity is calculated by dividing the number of moles of solute in the solution by the volume of the solution in liters.

$$\text{Molarity} = \frac{\text{Moles of solute}}{\text{Liters of solution}}$$

The symbol of molarity is M. A solution that contains 0.100 mol of NaCl in 1.00 L has a molarity of 0.100 M, and we would refer to the solution as 0.100 *molar* NaCl or as 0.100 M NaCl. The same concentration would result if we dissolved 0.0100 mol of NaCl in 0.100 L (100 mL) of solution, because the *ratio* of moles of solute to volume of solution is the same.

$$\frac{0.100 \text{ mol NaCl}}{1.00 \text{ L NaCl}} = \frac{0.0100 \text{ mol NaCl}}{0.100 \text{ L NaCl}} = 0.100 \text{ M NaCl}$$

Molarity is a tool that provides the conversion factors we need to convert between moles and volume (either in liters or milliliters). Consider, for example, a solution labeled 0.100 M NaCl. The unit M always translates to mean "moles per liter", so we can write

$$0.100 \text{ M NaCl} = \frac{0.100 \text{ mol NaCl}}{1.00 \text{ L solution}}$$

When working with solutions, it is much easier to measure the volume of the solution than the mass of the solute. Molarity can then be used to count the number of moles of solute in a given volume of a solution. Note that molarity has units of moles per liter. The product of the molarity of a solution times its volume in liters is, therefore, equal to the number of moles of solute dissolved in the solution.

$$\frac{\text{mol}}{\text{L}}\times\text{L}=\text{mol}$$

We can write this relationship in terms of the following generic equation, where M is molarity, V is volume in liters, and n is number of moles.

$$M\times V=n$$

It is possible to determine the number of atoms, ions or molecules in a mixture using measurements of density and volume if the percent by mass of each of the components in the mixture is known.

The chemicals used in the laboratory may be available in more concentrated form than required and must be *diluted* (made less concentrated) before being used. This is accomplished by adding more solvent to the solution, which spreads the solute through a larger volume and causes the concentration (the amount per unit volume) to decrease. For example, let us see how we would prepare 100.0 mL of 0.0400 M $K_2Cr_2O_7$ from 0.200 M $K_2Cr_2O_7$. The concentrated solution available has 0.20 M of $K_2Cr_2O_7$ in 1 L of water. For preparing 0.040 M solution, we would require 0.04 M of $K_2Cr_2O_7$ dissolved in 1 L of water. We can calculate the volume of 0.20 M solution required as

$$\frac{1000\text{ mL}}{0.2\text{ mol}}\times 0.04\text{ mol}=200\text{ mL}$$

For preparing 100 mL of solution, the amount required is

$$\frac{200\text{ mL}}{1000\text{ mL}}\times 100\text{ mL}=20\text{ mL}$$

Thus, 20 mL of 0.20 M solution may be taken and diluted to 100 mL for preparing a 100 mL solution.

During dilution, the amount of solute remains constant. This means that the product of molarity and volume, which equals the moles of solute, must be the same for both the concentrated and diluted solution.

$$\underbrace{\begin{array}{c}\text{Volume of dilute solution}\times M_{\text{dilute}}\\ \text{to be prepared}\end{array}}_{\text{Moles of solute in the dilute solution}}=\underbrace{\begin{array}{c}\text{Volume of concentrated solution}\times M_{\text{conc}}\\ \text{to be used}\end{array}}_{\text{Moles of solute in the concentrated solution}}\qquad(1.10)$$

or $$V_{\text{dil}}\cdot M_{\text{dil}}=V_{\text{conc}}\cdot M_{\text{conc}}$$

In the relation, any units can be used for volume provided that the volume units are the same on both sides of the equation. We thus normally solve dilution problems using *milliliters* directly in the equation

$$M_1V_1=M_2V_2$$

For preparation of 100.0 mL of 0.0400 M $K_2Cr_2O_7$ from 0.200 M $K_2Cr_2O_7$, we can use the relation as follows

$$0.2\times V_1=0.04\times 100$$

or $$V_1=\frac{0.04\times 100}{0.2}=20\text{ mL}$$

Note:

1. **Molarity of dilution:** The relation between molarity before and after dilution is given by
$$M_1V_1 = M_2V_2$$
2. **Molarity of mixing:** When three solutions (containing same solvent and solute) of molarity M_1, M_2, M_3 are mixed in volumes V_1, V_2, V_3 respectively, the molarity of mixing can be given as:
$$M_1V_1 + M_2V_2 + M_3V_3 = M_{\text{Total}}(V_1 + V_2 + V_3)$$

6. **Molality:** It is defined as the number of moles of solute per mass of solvent measured in kilograms. Thus,
$$\text{Molality} = \frac{\text{Number of moles of solute}}{\text{Mass of solvent in kg}}$$
The symbol of molality is small *m*. The total mass of the solution is still the sum of the mass of the solute and the mass of the solvent but this value is not used to determine the molality.

Note: Molality should not be confused with molarity whose symbol is capital *M*. Neither the mass nor volume of the solvent is used to define molarity. The combined volume of the two components (solute and solvent), the volume of the solution, is used for molarity.

7. **Strength of a solution:** It is defined as the amount of solute (in grams) dissolved per liter of solution. Mathematically, it is expressed as
$$S = \frac{\text{Weight of solute (g)}}{\text{Volume of solution (L)}}$$

Relation between Stoichiometric Quantities

1. **Relation between mole fraction and molality:**
$$x_A = \frac{n_A}{n_A + n_B} \text{ and } x_B = \frac{n_B}{n_A + n_B}$$
$$\frac{x_A}{x_B} = \frac{n_A}{n_B} = \frac{\text{Moles of solute}}{\text{Moles of solvent}} = \frac{w_A \times M_B}{w_B \times M_A}$$
$$\frac{x_A \times 1000}{x_B \times M_B} = \frac{w_A \times 1000}{w_B \times M_A} = m \Rightarrow \frac{x_A \times 1000}{(1 - x_A)M_B} = m$$
2. **Relationship between molality and molarity:**
$$\frac{1}{m} = \frac{d}{M} - \frac{M_B}{1000}$$
where d = density of solution, m = molality, M = molarity and M_B = molar mass of solute
3. **Relation between molarity and mole fraction:** Let M be the molarity of solution, and x_A and x_B be mole fractions of solvent and solute, respectively. When n_A and n_B moles of solvent and solute are mixed to form a solution, then mass of solution is $n_AM_A + n_BM_B$ where M_A and M_B are molar masses of solvent and solute, respectively. Then,
$$\text{Volume of solution} = \frac{\text{Mass}}{\text{Density}} = \frac{(n_AM_A + n_BM_B)}{d}$$
$$\text{Molarity} = \text{Number of moles of solute} \times \frac{1000}{\text{Volume of solution}}$$
$$M = n_B \times \frac{1000 \times d}{(n_AM_A + n_BM_B)}$$
Dividing both numerator and denominator by $(n_A + n_B)$, we get
$$M = \frac{x_B \times 1000 \times \rho}{x_AM_A + x_BM_B}$$

Solved Example 1-54

Find the molarity of 1 L of water. Given: $d = 1000$ kg m^{-3} **(IIT-JEE 2003)**

Solution

Molarity is defined as the number of moles of solute present/volume of solution in liters.

Given, 1 L of water = 1 kg = 1000 g (because density = 1000 kg m^{-3}). Therefore, the number of moles of solute present

$$= \frac{1000(\text{given mass})}{18(\text{molecular mass of water})} = 55.55 \text{ mol of } H_2O$$

So, the molarity is 55.55 mol/1 L = 55.55 M.

Solved Example 1-55

Calculate the weight of MnO_2 and the volume of HCl of specific gravity 1.2 g mL^{-1} and 4% nature by weight needed to produce 1.78 L of Cl_2 at STP by the reaction.

Solution

The reaction involved is $MnO_2 + 4HCl \rightarrow MnCl_2 + 2H_2O + Cl_2$

$$\text{The number of moles of } Cl_2 = \frac{1.78}{22.4} = 0.07946 \text{ mol}$$

The number of moles of MnO_2 = 0.07946 mol

Therefore, mass of MnO_2 = number of moles × molecular weight = 0.0794 × 87= 6.913 g

Now, the number of moles of HCl = 4 × 0.07946 = 0.3178 mol

Thus, the mass of HCl = 0.3176 × 36.5.

Now, let the volume of HCl = V mL, then

$$V \times 1.2 \times \frac{4}{100} = 0.317 \times 36.5$$

$$V = \frac{0.317 \times 36.5 \times 100}{1.2 \times 4} = 241.05 \text{ mL}$$

1.7 | MISCELLANEOUS APPLICATION OF MOLE CONCEPT: GRAVIMETRIC ANALYSIS

Gravimetric analysis is a quantitative analysis based on the measurement of weight by the process of isolating and weighing an element or compound in the pure form. Gravimetric analysis is concerned with the transformation of element to be determined into a pure and stable state which is suitable for weighing. The weight of element is calculated from the known formula of the compound and relative masses of its constituents.

There are two main methods for carrying out this analysis – volatilization and precipitation.

1. **Precipitation method:** In precipitation method, the substance is dissolved into a solvent and converted into a precipitate by using a precipitating agent. The precipitate is filtered, dried, made free of contamination and converted into a compound of known stoichiometric composition. The compound is weighed and the amount of analyte is determined.

   The important criteria are that the precipitating agents should be specific for that compound, so that it does not precipitate out the impurities in the sample. The precipitate should form quantitatively in a short period of time, should be stable and have low solubility in the solvent. It should not react with moisture and be stable to heat treatment.

   Some important precipitating agents used are silver nitrate, potassium dichromate, ammonium molybdate and organic agents such as oxalates, dimethylglyoxime (DMG), anthranilic acid, etc. Some examples of precipitation method are estimation of nickel by precipitation as Ni–DMG complex, lead as $PbCrO_4$, copper as CuSCN, etc.
2. **Volatilization method:** In volatilization method, the sample is either dried or heated to a separate volatile and non-volatile content. The non-volatile residue is weighed and loss of weight in the sample is the measure of volatile material present. This method is used for the determination of dissolved impurities in water. Another use is in the determination of amount of carbon dioxide in carbonate ores. A known amount of ore is heated, and metal residue obtained on volatilization of carbon dioxide. The amount of carbonate is determined from the difference in weight of sample and metal residue.

Solved Example 1-56

4.08 g of a mixture of BaO and an unknown carbonate MCO_3 was heated strongly. The residue weighed 3.67 g. This was dissolved in 100 mL of 1 N HCl. The excess of acid required 16 mL of 2.5 N NaOH for complete neutralization. Identify the metal M.

Solution

On heating BaO does not decompose. Only carbonate decomposes as follows.

$$MCO_3 \rightarrow MO(s) + CO_2(g)$$

1 mol of $MCO_3 \equiv$ 1 mol of MO $\equiv$ 1 mol of CO_2
Loss in weight on heating is due to the loss of CO_2.
Weight of $CO_2 = 4.08 - 3.64 = 0.44$ g $\equiv 0.01$ mol of CO_2
From stoichiometry, we have
Moles of MO = moles of $MCO_3 = 0.01$ gram equiv. of MO = 2 (0.01)
(where gram equiv. = acidity moles)
Let x be the atomic weight of M. Then molecular mass of $MCO_3 = x + 60 \Rightarrow$ mass of BaO $= 4.08 - 0.01\ (x + 60)$.
Now both the oxides, BaO and MO will react with HCl.
At neutralization stage,
milliequiv. of oxides = milliequiv. of HCl.

milliequiv. of HCl used for oxide $= 1 \times 100 - 2.5 \times 16 = 60$

Now, milliequiv. of MO + milliequiv. of BaO

$$= \left[2(0.01) + \frac{4.08 - 0.01(x+60)}{154/2}\right] \times 1000 = 60$$

$$77 \times 0.02 + 4.68 - 0.01x = \frac{60 \times 77}{1000}$$

$$\Rightarrow 0.01x = 4.62 - 3.48 - 1.54 \Rightarrow x = 40 \text{ u}$$

Hence, the metal M having atomic weight 40 u is calcium (Ca).

Solved Example 1-57

Igniting MnO_2 in air converts it quantitatively to Mn_3O_4. A sample of pyrolusite is of the following composition: $MnO_2 = 80\%$ and other inert constituents = 15% and rest bearing H_2O. The sample is ignited to constant weight. What is the percentage of Mn in the ignited sample?

Solution

The reaction involved is $3MnO_2 \rightarrow Mn_3O_4 + O_2$. From stoichiometry, we have:

3 mol of $MnO_2 \equiv$ 1 mol of $Mn_3O_4 \equiv$ 3 mol of Mn
1 mol of $MnO_2 \equiv$ 1/3 mol of Mn_3O_4

Let 100 g of pyrolusite sample be taken. Then grams of $MnO_2 = 80$ g $\Rightarrow$ moles of $MnO_2 = 80/87$

From stoichiometry, we have

$$\text{Moles of } Mn_3O_4 = \frac{1}{3}\left(\frac{80}{87}\right)$$

$$\text{Moles of Mn} = \frac{80}{87}$$

$$\text{Grams of Mn} = \frac{80}{87} \times 55 = 50.57 \text{ g}$$

$$\text{Grams of } Mn_3O_4 = \frac{1}{3}\left(\frac{80}{87}\right) \times 229 = 70.19$$

Total weight of ignited sample = 70.19 + 15 (SiO_2 and inert matter) = 85.19

$$\text{Therefore, \%Mn} = \frac{50.57}{85.19} \times 100 = 59.36\%$$

SOLVED OBJECTIVE QUESTIONS FROM PREVIOUS YEAR PAPERS

1. A 2 L solution contains 0.04 mol of each of $[Co(NH_3)_5SO_4]Br$ and $[Co(NH_3)_5Br]SO_4$. To 1 L of this solution, excess of $AgNO_3$ is added. To the remaining solution, excess of $BaCl_2$ is added. The amounts of precipitated salts, respectively, are **(IIT-JEE 2003)**

(A) 0.01 mol, 0.01 mol
(B) 0.01 mol, 0.02 mol
(C) 0.02 mol, 0.01 mol
(D) 0.02 mol, 0.02 mol

Solution

(D) Given that 2 L solution contains 0.04 mol each of $[Co(NH_3)_5SO_4]Br$ and $[Co(NH_3)_5Br]SO_4$. Therefore, the concentration of $[Co(NH_3)_5SO_4]Br$ and $[Co(NH_3)_5Br]SO_4$ in 2 L of solution contains 0.02 mol L^{-1}.
$[Co(NH_3)_5SO_4]Br$ has ionizable Br^- ions and $[Co(NH_3)_5Br]SO_4$ has ionizable SO_4^{2-} ions. The reactions involved are as follows:

$$\underset{\text{Excess}}{Ag^+} + \underset{0.02}{Br^-} \rightarrow \underset{0.02}{AgBr}$$

$$\underset{\text{Excess}}{Ba^{2+}} + \underset{0.02}{SO_4^{2-}} \rightarrow \underset{0.02}{BaSO_4}$$

2. Which of the following has maximum number of atoms? **(IIT-JEE 2003)**

(A) 24 g of C (Mol. wt. = 12 g mol^{-1})
(B) 23 g of Na (Mol. wt. = 23 g mol^{-1})
(C) 48 g of S (Mol. wt. = 32 g mol^{-1})
(D) 108 g of Ag (Mol. wt. = 108 g mol^{-1})

Solution

(A) 24 g carbon amounts to 24/12 = 2 mol, that is, 2 × 6.023×10^{23} atoms, whereas (B), (C) and (D) amount to 1 mol, 1.5 mol and 1 mol, respectively.

3. Given that the abundances of isotopes ^{54}Fe, ^{56}Fe and ^{57}Fe are 5%, 90% and 5%, respectively. The atomic mass of Fe is **(IIT-JEE 2009)**

(A) 55.85
(B) 55.95
(C) 55.75
(D) 56.75

Solution

(B) Atomic mass of iron $= \dfrac{54\times 5+56\times 90+57\times 5}{100} = 55.95$ u

4. Among the following, the intensive property is (properties are) **(IIT-JEE 2010)**

(A) molar conductivity
(B) electromotive force
(C) resistance
(D) heat capacity

Solution

(A), (B) Resistance and heat capacity are mass dependent properties, hence they are extensive properties.

5. A student performs a titration with different burettes and finds titre value of 25.2 mL, 25.25 mL and 25.0 mL. The number of significant figures in the average titre value is __________. **(IIT-JEE 2010)**

Solution

(3) The average titre value is (25.2 + 25.25 + 25.0)/3 = 25.15 mL = 25.2 mL (according to addition of significant figures) which means there are three significant figures.

6. Silver (atomic weight = 108 mol^{-1}) has a density of 10.5 g cm^{-3}. The number of silver atoms on a surface of area 10^{-12} m^2 can be expressed in scientific notation as $y \times 10^x$. The value of x is __________. **(IIT-JEE 2010)**

Solution

(7) We know that density = mass/volume. Given that density = 10.5 g cm^{-3}. This means 10.5 g of Ag is present in 1 cm^3.
Thus, number of atoms of Ag present in one cm^3 = $10.5/108 \times N_A$
In 1 cm, number of atoms of Ag = $(10.5/108 \times N_A)^{1/3}$
In 1 cm^2, number of atoms of Ag = $(10.5/108 \times N_A)^{2/3}$
In 10^{-8} cm^2, number of atoms of Ag = $(10.5/108 \times N_A)^{2/3} \times 10^{-8} = (1.05 \times 6.022 \times 10^{24}/10^8) \times 10^{-8} = 1.5 \times 10^7$.
Hence, $x = 7$.

7. Dissolving 120 g of urea (mol. wt. = 60) in 1000 g of water gave a solution of density 1.15 g mL^{-1}. The molarity of the solution is __________. **(IIT-JEE 2011)**

(A) 1.78 M
(B) 2.00 M
(C) 2.05 M
(D) 2.22 M

Solution

(C) Since the solution consists of both urea and water, so the mass of the solution = 1000 + 12 = 1012 g.
Volume of solution = mass of solution/density of solution = 1012/1.15 = 973.91 g mL^{-1}.
Now, Molarity = Number of moles/Volume of solution in liters, where number of moles = 120/60 = 2. Thus, Molarity = 2/0.974 = 2.05 M.

8. Reaction of Br_2 with Na_2CO_3 in aqueous solution gives sodium bromide and sodium bromate with evolution of CO_2 gas. The number of sodium bromide molecules involve in the balanced chemical equation is __________. **(IIT-JEE 2011)**

Solution

(5) The balanced chemical equation is:

$$3Na_2CO_3 + 3Br_2 \rightarrow 5NaBr + NaBrO_3 + 3CO_2$$

9. The volume (in mL) of 0.1 M $AgNO_3$ required for complete precipitation of chloride ions present in 30 mL of 0.01 M solution of $[Cr(H_2O)_5Cl]Cl_2$, as silver chloride is close to __________. **(IIT-JEE 2011)**

Solution

(6) The reaction involved is

$$\begin{aligned} &2AgNO_3 + [Cr(H_2O)_5Cl]Cl_2 \\ &\quad \rightarrow 2AgCl + [Cr(H_2O)_5Cl](NO_3)_2 \end{aligned}$$

Using molarity equation, we get

$$(M \times n \times V)_{AgNO_3} = (M \times n \times V)_{[Cr(H_2O)_5Cl]Cl_2}$$

$$0.1 \times 1 \times V = 0.01 \times 2 \times 30 \Rightarrow V = 6 \text{ mL}$$

10. 29.2% (*w*/*w*) HCl stock solution has density of 1.25 g mL^{-1}. The molecular weight of HCl is 36.5 g mol^{-1}. The volume (mL) of stock solution required to prepare a 200 mL solution of 0.4 M HCl is __________. **(IIT-JEE 2012)**

Solution

(8) Given that density of solution = 1.25 g mL^{-1}.
29.2% HCl means 29.2 g of HCl in 100 g of the solution
Density of the solution = Mass of the solution/Volume of the solution ⇒ $V = 100/1.25$ mL.
Now, molarity of the solution =

$$\frac{\text{Number of moles of HCl}}{\text{Volume of solution}} \times 1000 = \frac{29.2/36.5}{100/1.25} \times 1000 = 10 \text{ M}$$

Using molarity equation $M_1V_1 = M_2V_2$, we get

$$10 \times V = 0.4 \times 200 \Rightarrow V = 8 \text{ mL}$$

11. A compound H_2X with molar weight of 80 g is dissolved in a solvent having density of 0.4 g mL^{-1}. Assuming no change in volume upon dissolution, the molality of a 3.2 molar solution is _____. **(JEE Advanced 2014)**

Solution

(8) Given that molarity is 3.2 M, so 3.2 moles are dissolved in 1000 ml of solution. Now,

$$\text{Mass} = \text{Density} \times \text{Volume} \Rightarrow 0.4 \times 1000 = 400 \text{ g}$$

Therefore, molality is $m = \dfrac{3.2}{400} \times 1000 = 8$ molal

12. Three moles of B_2H_6 are completely reacted with methanol. The number of moles of boron containing product formed is _____. **(JEE Advanced 2015)**

Solution

(6) The reaction is

$$B_2H_6 + 6CH_3OH \rightarrow 2B(OCH_3)_3 + 6H_2$$

From the reaction, 1 mol of B_2H_6 reacts with 6 mol of CH_3OH to produce 2 mol of $B(OCH_3)_3$.

Therefore, 3 mol of B_2H_6 would react with 18 mol of CH_3OH to produce 6 mol of $B(OCH_3)_3$.

13. 25 mL of a solution of barium hydroxide on titration with 0.1 M solution of hydrochloric acid gave a liter value of 35 mL. The morality of barium hydroxide solution was **(AIEEE 2003)**

(A) 0.07 (B) 0.14
(C) 0.28 (D) 0.35

Solution

(B) Using the molarity equation, $M_1V_1 = M_2V_2$ (HCl), we get

$$M_1 = 0.1 \times \frac{35}{25} = 0.14$$

14. 6.02×10^{20} molecules of urea are present in 100 mL of its solution. The concentration of urea solution is **(AIEEE 2004)**

(A) 0.001 M (B) 0.1 M
(B) 0.02 M (D) 0.01 M

Solution

(D) 6.02×10^{23} molecule makes 1 mol. So, 6.02×10^{20} molecule makes 1/1000 (10^{-3}) mol. The concentration is

$$\text{Concentration} = \frac{\text{Number of moles}}{\text{Volume (in liters)}}$$
$$= \frac{10^{-3}/100}{1000} = 0.01 \text{ M}$$

15. Two solutions of a substance (non-electrolyte) are mixed in the following manner. 480 mL of 1.5 M first solution + 520 mL of 1.2 M second solution. What is the molarity of the final mixture? **(AIEEE 2005)**

(A) 1.20 M (B) 1.50 M
(B) 1.344 M (D) 2.70 M

Solution

(C) According to molarity equation $M_3(V_1 + V_2) = M_1V_1 + M_2V_2$, we have

$$M_3 = \frac{(480 \times 1.5 + 520 \times 1.2)}{1000} = 1.344 \text{ M}$$

16. If we consider that 1/6, in place of 1/12, mass of carbon atom is taken to be the relative atomic mass unit, the mass of one mole of substance will **(AIEEE 2005)**

(A) decrease twice
(B) increase two fold
(C) remain unchanged
(D) be a function of the molecular mass of the substance

Solution

(A) The relative atomic mass is expressed as

$$\text{Relative atomic mass} = \frac{\text{Mass of one atom of the element}}{1/12\text{th part of the mass of one atom of carbon}}$$

If 1/12 is replaced with 1/6, then we have

$$\text{Relative atomic mass} = \frac{\text{Mass of one atom of the element}}{1/6\text{th part of the mass of one atom of carbon}}$$

Now, 1 mol of substance = 6.023×10^{23} atoms. If we consider the mass of 1 mol in kg then it will remain the same, and in relative atomic mass units, it will become half times the original.

17. How many moles of magnesium phosphate, $Mg_3(PO_4)_2$ will contain 0.25 mole of oxygen atoms? **(AIEEE 2006)**

(A) 0.02 (B) 3.125×10^{-2}
(C) 1.25×10^{-2} (D) 2.5×10^{-2}

Solution

(B) One mole of $Mg_3(PO_4)_2$ contains 8 oxygen atoms. n moles contain $8n$ oxygen atoms. Therefore for 0.25 mol,

$$0.25 = 8n \Rightarrow n = \frac{0.25}{8} = 3.125 \times 10^{-2}$$

18. Density of a 2.05 M solution of acetic acid in water is 1.02 g mL^{-1}. The molality of the solution is **(AIEEE 2006)**

(A) 1.14 mol kg^{-1} (B) 3.28 mol kg^{-1}
(C) 2.28 mol kg^{-1} (D) 0.44 mol kg^{-1}

Solution

(C) Molality is given by

$$\text{Molality} = \frac{\text{Number of moles}}{\text{kg of solvent}} = \frac{(m/w)\text{ moles}}{\text{kg of solvent}}$$

Now, assume 1 L of solution. We need to convert the molarity units from mol L^{-1} to mol kg^{-1}.

$$\text{Molality} = \frac{2.05 \text{ mol}}{1 \text{ L}} \times \frac{1 \text{ mL}}{1.02 \text{ g}} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{1000 \text{ g}}{1 \text{ kg}}$$
$$= 2.0098 \text{ mol/kg}$$

19. The density (in g mL^{-1}) of a 3.60 M sulphuric acid solution that is 29% H_2SO_4 (molar mass = 98 g mol^{-1}) by mass will be **(AIEEE 2007)**

(A) 1.45 (B) 1.64
(C) 1.88 (D) 1.22

Solution

(D) Let the density of solution be ρ. Molarity of solution given = 3.6 M, that is 1 L of solution contains 3.6 mol of H_2SO_4 or 1 L of solution contains 3.6 × 98 g of H_2SO_4. Since the solution is 29% by mass,
100 g solution contains 29 g H_2SO_4
100/ρ mL solution contains 29 g H_2SO_4
1000 mL solution contains 3.6 × 98 g H_2SO_4
Therefore,

$$3.6\times 98=\frac{29\times\rho}{100}\times 1000$$

Solving, we get $\rho = 1.22$ g mL^{-1}.

20. A 5.2 molal aqueous solution of methyl alcohol CH_3OH is supplied. What is the mole fraction of methyl alcohol in the solution? **(AIEEE 2011)**

(A) 0.190 (B) 0.086
(C) 0.050 (D) 0.100

Solution

(B) Mole fraction of methyl alcohol = number of moles of methyl alcohol/total number of moles (i.e., both $CH_3OH + H_2O$)

$$\text{Mole fraction}=\frac{m_1}{m_1+\frac{1000}{18}}=\frac{5.2}{5.2+\frac{1000}{18}}=0.086$$

21. The density of a solution prepared by dissolving 120 g of urea (molar mass = 60 u) in 1000 g of water is 1.15 g mL^{-1}. The molarity of the solution is **(AIEEE 2012)**

(A) 0.50 M (B) 1.78 M
(C) 1.02 M (D) 2.05 M

Solution

(D) Molarity of solution is defined as

$$M=\frac{\text{Number of moles of urea}}{\text{Volume of solution in mL}}\times 1000$$

Now, number of moles of urea

$$=\frac{\text{Given mass of urea}}{\text{Molar mass of urea}}=\frac{120}{60}$$

Also, density of solution

= Mass of solution/Volume of solution (1)

where mass of solution = mass of urea + mass of water
= 120 + 1000 = 1120 g

Substituting values in Eq. (1), we get

$$1.15=\frac{1120}{\text{Volume}}\Rightarrow \text{Volume}=\frac{1120}{1.15}=973.9\text{ mL}$$

Therefore,

$$M=\frac{120/60}{973.9}\times 1000=2.05\text{ M}$$

22. The molarity of a solution obtained by mixing 750 mL of 0.5 M HCl with 250 mL of 2 M HCl will be **(JEE Main 2013)**

(A) 1.00 M (B) 1.75 M
(C) 0.975 M (D) 0.875 M

Solution

(D) $M_1V_1+M_2V_2=MV\Rightarrow M=\dfrac{M_1V_1+M_2V_2}{V}$

$$=\frac{0.5\times 750+2\times 250}{1000}\Rightarrow M=0.875$$

23. The ratio of masses of oxygen and nitrogen in a particular gaseous mixture is 1:4. The ratio of number of their molecule is **(JEE Main 2014)**

(A) 1:4 (B) 7:32
(C) 1:8 (D) 3:16

Solution

(B) Let the mass of oxygen be x and that of nitrogen be $4x$.

So, the number of moles of oxygen is $x/32$ and that of nitrogen is $4x/28 = x/7$

The required ratio is $\dfrac{x}{32}\times\dfrac{7}{x}=\dfrac{7}{32}$

24. 3 g of activated charcoal was added to 50 mL of acetic acid solution (0.06 N) in a flask. After an hour it was filtered and the strength of the filtrate was found to be 0.042 N. The amount of acetic acid adsorbed (per gram of charcoal) is: **(JEE Main 2014)**

(A) 36 mg (B) 42 mg
(C) 54 mg (D) 18 mg

Solution

(D) Initial moles of $CH_3COOH = 0.06\times 50$

Final moles of $CH_3COOH = 0.042\times 50$

So, the mass of CH_3COOH adsorbed per gram of charcoal

$$=\frac{(0.06-0.042)\times 50\times 10^{-3}\times 60\times 10^{3}}{3}=18\text{ mg}$$

25. The molecular formula of a commercial resin used for exchanging ions in water softening is $C_8H_7SO_3Na$ (Mol. Wt. 206). What would be the maximum uptake of Ca^{2+} ions by the resin when expressed in mole per gram resign? **(JEE Main 2015)**

(A) $\dfrac{1}{206}$ (B) $\dfrac{2}{309}$
(C) $\dfrac{1}{412}$ (D) $\dfrac{1}{103}$

Solution

(C) $\underset{1/206\text{ mol}}{2C_8H_7SO_3Na}+\underset{1/412\text{ mol}}{Ca^{2+}}\rightarrow (C_8H_7SO_3)_2Ca+2Na^{+}$

Maximum uptake of Ca^{2+} ions $=\dfrac{1}{206\times 2}=\dfrac{1}{412}$

REVIEW QUESTIONS

1. Define mass and weight. How are they measured?

2. What does symbol S.I. signify? Name the seven basic S.I. units.

3. Explain why chemists might find it more useful to describe concentrated H_2SO_4 as a solution that contains 18.0 mol of solute per liter instead of as a solution that is 96.0% H_2SO_4 by mass.

4. What is the difference between the mass of a molecule and gram molecular mass?

5. Calculate the amount of carbon dioxide that could be produced when
- **(a)** one mole of carbon is burnt in air.
- **(b)** one mole of carbon is burnt in 16 g of dioxygen.
- **(c)** two moles of carbon are burnt in 16 g of dioxygen.

6. n gram of a substance X reacts with m g of substance Y to form p g of substance R and q g of substance S. This reaction can be represented as follows: $X + Y = R + S$. What is the relation which can be established in the amounts of the reactants and the products?

7. A gold-colored metal object has a mass of 365 g and a volume of 22.12 cm^3. Is the object composed of pure gold?

8. Why must measurements always be written with units? What is the meaning of each of the following prefixes? **(a)** centi-, **(b)** milli-, **(c)** kilo-, **(d)** micro-, **(e)** nano-, **(f)** pico- and **(g)** mega-

9. State the rules to follow in rounding off a number.

10. Suppose 2.0 mol of $H_2(g)$ is mixed with 1.0 mol of $O_2(g)$ and allowed to react as shown below.

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$$

- **(a)** How many atoms of H and O are initially present?
- **(b)** How many atoms of H and O will there be in the product?
- **(c)** How many molecules of H_2 and O_2 were initially present?
- **(d)** How many molecules of H_2O were formed?

11. The following data are obtained when dinitrogen and dioxygen react together to form different compounds:

Mass of dinitrogen	Mass of dioxygen
(A) 14 g	16 g
(B) 14 g	32 g
(C) 28 g	32 g
(D) 28 g	80 g

Which law of chemical combination is obeyed by the above experimental data? Give its statement.

12. Describe what you need to do in the laboratory to test **(a)** the law of conservation of mass, **(b)** the law of definite proportions and **(c)** the law of multiple proportions.

13. What is meant by the statement "1 g of Mg is burnt in a closed vessel that contains 0.5 g of O_2"?

14. State true or false and give reasons: "Average atomic mass of an element depends mainly on the heavier isotope."

15. Give reasons for the following:
- **(a)** Both 106 g of sodium carbonate and 12 g of carbon have same number of carbon atoms.
- **(b)** The volume occupied by one molecule of water, if density of water is 1.0×10^3 kg m^{-3} is 2.99×10^{-23} mL.

16. Identify the compound and mixture from the following: cinnabar and brass.

17. What are the number of significant digits in Avogadro's constant?

NUMERICAL PROBLEMS

1. The interatomic distance in the hydrogen molecule is given as 0.74 Å. What is this distance in nanometers, micrometers and millimeters?

2. Calculate the number of moles of nitrogen dioxide NO_2 that could be prepared from 0.35 mol of nitrogen oxide and 0.25 mol of oxygen.

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

3. β-Carotene is the pro-vitamin from which nature builds vitamin A. Calculate the molecular formula for β-carotene if the compound is 89.49% C and 10.51% H by mass and its molecular weight is 536.89 g mol^{-1}.

4. Urea (H_2NCONH_2) is manufactured by passing $CO_2(g)$ through ammonia solution followed by crystallization. CO_2 for the above reaction is prepared by combustion of hydrocarbon. If combustion of 236 kg of a saturated hydrocarbon (C_nH_{2n+2}) produces as much CO_2 as required for production of 999.6 kg urea then what is the molecular formula of hydrocarbon?

5. In an experiment, 10 cm^3 of an organic compound in the gaseous state were sparked with an excess of oxygen. 20 cm^3 of carbon dioxide and 5 cm^3 of nitrogen were obtained among the products. All gas volumes were measured at the same temperature and pressure. What are the possible molecular formulas that would fit these data?

6. Sulphuric acid reacts with sodium hydroxide as follows:

$$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$$

When 1 L of 0.1 M sulphuric acid solution is allowed to react with 1 L of 0.1 M sodium hydroxide solution, what is the amount of sodium sulphate formed and its molarity in the solution?

7. If haemoglobin (molecular weight ≅ 67200) contains 0.33% of iron by weight, then what is the number of iron atoms present in one molecule of haemoglobin?

8. When 1 L of CO_2 is heated with graphite, the volume of the gases collected is 1.5 L. Calculate the number of moles of CO produced at STP.

9. X and Y are two elements which form X_2Y_3 and X_3Y_4. If 0.20 mol of X_2Y_3 weighs 32.0 g and 0.4 mol of X_3Y_4 weighs 92.8 g, what are the atomic masses of X and Y?

10. What will be the composition of residual mixture if 30 g of Mg combines with 30 g of oxygen?

(a) 40 g MgO + 20 g O_2
(b) 45 g MgO + 15 g O_2
(c) 50 g MgO + 10 g O_2
(d) 60 g MgO only.

11. Manganese trifluoride can be prepared by the following reaction:

$$MnI_2(s) + F_2(g) \rightarrow MnF_3 + IF_5$$

What is minimum number of grams of F_2 that must be used to react with 12.0 g of MnI_2 if overall yield of MnF_3 is no more than 75%?

ADDITIONAL OBJECTIVE QUESTIONS

Single Correct Choice Type

1. How much quantity of zinc will have to be reacted with excess of dilute HCl solution to produce sufficient hydrogen gas for completely reacting with the oxygen obtained by decomposing 5.104 g of potassium chlorate?

(A) 8.124 g
(B) 81.24 g
(C) 0.08 g
(D) 812.4 g

2. Octane is a component of gasoline. Incomplete combustion of octane produces some CO along with CO_2 and H_2O, which reduces efficiency of engine. In a certain test run, 1.0 gallon of octane is burned and total mass of CO, CO_2 and H_2O produced was found to be 11.53 kg. The efficiency of the engine would be [density of octane is 0.7 g cm^{-3}]

(A) 80%
(B) 95.5%
(C) 40.2%
(D) 51.2%

3. The number of moles of $CaCl_2$ needed to react with excess of $AgNO_3$ to produce 4.31 g of AgCl is

(A) 0.030
(B) 0.015
(C) 0.045
(D) 0.060

4. Chlorine is prepared in the laboratory by treating manganese dioxide (MnO_2) with aqueous hydrochloric acid according to the reaction

$$4HCl(aq) + MnO_2(s) \rightarrow 2H_2O(l) + MnCl_2(aq) + Cl_2(g)$$

The grams of HCl react with 5.0 g of manganese dioxide will be [atomic mass of Mn = 55 u]

(A) 84 g
(B) 0.84 g
(C) 8.4 g
(D) 4.2 g

5. Copper reacts with dilute nitric acid according to the following equation:

$$3Cu(s) + 8HNO_3(aq) \rightarrow 3Cu(NO_3)_2(aq) + 2NO(g) + 4H_2O(l)$$

If a copper coin weighing 3.045 g is dissolved in a small amount of nitric acid and the resultant solution is diluted to 50.0 mL with water, what is the molarity of the $Cu(NO_3)_2$?

(A) 0.958 M
(B) 0.278 M
(C) 0.145 M
(D) 0.312 M

6. 8 g of sulphur is burnt to form SO_2 which is oxidized by Cl_2 water. The solution is treated with $BaCl_2$ solution. The amount of $BaSO_4$ precipitate is

(A) 1 mol
(B) 0.5 mol
(C) 0.24 mol
(D) 0.25 mol

7. The sterile saline solution used to rinse contact lenses can be made by dissolving 400 mg of NaCl in sterile water and diluting to 100 mL. What is the molarity of the solution?

(A) 0.0685 M
(B) 0.0312 M
(C) 0.0212 M
(D) 0.0418 M

8. Titanium metal is obtained from the mineral rutile, TiO_2. How many kilograms of rutile are needed to produce 100.0 kg of Ti?

(A) 166.8 kg
(B) 132.4 kg
(C) 11.4 kg
(D) 14.3 kg

9. A sample of tap water contains 366 ppm of HCO_3^- ions with Ca^{2+} ion. Now it is removed by Clarke's method by addition of $Ca(OH)_2$. Then what minimum mass of $Ca(OH)_2$ will be required to remove HCO_3^- ions completely from 500 g of same tap water sample?

(A) 1 g
(B) 0.4 g
(C) 0.222 g
(D) 0.111 g

10. An inorganic substance has the following composition: N = 35%, H = 5%, O = 60%. On being heated, it yielded a gaseous compound containing N = 63.3% and O = 36.37%. Which of the following reaction can be suggested based on the given data?

(A) $2HNO_3 \rightarrow N_2O_5 + H_2O$
(B) $NH_2OH + HONO \rightarrow N_2O + 2H_2O$
(C) $NH_4NO_3 \rightarrow N_2O + 2H_2O$
(D) $2HNO_2 \rightarrow N_2O_3 + H_2O$

11. 55 g of $Ba(MnO_4)_2$ sample containing inert impurity is completely reacting with 100 mL of 56 volume strength of H_2O_2, then what will be the percentage purity of $Ba(MnO_4)_2$ in the sample? (Ba – 137 u, Mn – 55 u)

(A) 40%
(B) 25%
(C) 10%
(D) 68.18%

12. The simplest formula of a compound containing 50% of element X (atomic mass 10) and 50% of element Y (atomic mass 20) is

(A) XY
(B) X_2Y
(C) XY_3
(D) X^2Y_3

13. Hydrochloric acid solutions A and B have concentration of 0.5 N and 0.1 N, respectively. The volume of solution A and B required to make 2 L of 0.2 N hydrochloric are:

(A) 0.5 L of A + 1.5 L of B
(B) 1.0 L of A + 1.0 L of B
(C) 1.5 L of A + 0.5 L of B
(D) 0.75 L of A + 1.25 L of B

14. The density of 1 M solution of NaCl is 1.0585 g mL^{-1}. The molality of the solution is
(A) 1.0585 molal (B) 1.00 molal
(C) 0.10 molal (D) 0.0585 molal

15. H_3PO_4 is a tribasic acid and one of its salt is NaH_2PO_4. What volume of 1 M NaOH solution should be added to 12 g of NaH_2PO_4 to convert it into Na_3PO_4?
(A) 100 mL (B) 200 mL
(C) 80 mL (D) 300 mL

16. A sample of hard water contains 1 mg $CaCl_2$ and 1 mg $MgCl_2$ per liter. Calculate the hardness of water in terms of $CaCO_3$ present in per 10^6 parts of water.
(A) 215 ppm (B) 2.15 ppm
(C) 105 ppm (D) None of these

17. A 10.0 g sample of a mixture of calcium and sodium chloride is treated with Na_2CO_3 to precipitate the calcium as calcium carbonate. This $CaCO_3$ is heated to convert all the calcium into CaO and final mass of CaO is 1.62 g. The % by mass of $CaCl_2$ in the original mixture is
(A) 15.2% (B) 32.1%
(C) 21.8% (D) 11.7%

18. A sample of hard water contains 244 ppm of HCO_3^- ions. What is the minimum mass of CaO required to remove ions completely from 1 kg of such a water sample ?
(A) 56 mg (B) 112 mg
(C) 168 mg (D) 244 mg

19. A metal oxide has the formula Z_2O_3. It can be reduced by hydrogen to give free metal and water. 0.16 g of the metal oxide required 6 mg of hydrogen for complete reduction. The atomic weight of the metal is
(A) 27.9 (B) 159.6
(C) 79.8 (D) 55.8

20. P and Q are two elements which from P_2Q_3 and PQ_2. If 0.15 mol of P_2Q_3 weights 15.9 g and 0.15 mol of PQ_2 weights 9.3 g, the atomic weight of P and Q is, respectively
(A) 18, 26 (B) 26, 18
(C) 13, 9 (D) none of these

Multiple Correct Choice Type

1. Which of the following solutions have the same concentration?
(A) 20 g of NaOH in 200 mL of solution.
(B) 0.5 mol of KCl in 200 mL of solution.
(C) 40 g of NaOH in 100 mL of solution.
(D) 20 g of KOH in 200 mL of solution.

2. Which of the following quantities are dependent on temperature?
(A) Molarity (B) Normality
(C) Molality (D) Mole fraction

3. PF_3 reacts with XeF_4 to give PF_5.

$$2PF_3(g) + XeF_4(s) \rightarrow 2PF_5(g) + Xe(g)$$

If 100.0 g of PF_3 and 50.0 of XeF_4 react, then which of the following statements is true?
(A) XeF_4 is the limiting reagent.
(B) PF_3 is the limiting reagent.
(C) 1.137 mol of PF_5 are produced.
(D) 0.482 mol of PF_5 are produced.

4. 1 mol of H_2SO_4 will exactly neutralize
(A) 2 mol of ammonia (B) 1 mol of $Ca(OH)_2$
(C) 0.5 mol of $Ba(OH)_2$ (D) 2 mol NaOH

Assertion–Reasoning Type

Choose the correct option from the following:
(A) Statements 1 and 2 are True; Statement 2 is the correct explanation of Statement 1
(B) Statements 1 and 2 are True; Statement 2 is not the correct explanation of Statement 1
(C) Statement 1 is True, Statement 2 is False.
(D) Statements 1 is False, Statement 2 is True.

1. **Statement 1:** Molecular mass = 2 × Vapor density.

Statement 2: Vapor density is the mass ratio of 1 mol of vapor to that of hydrogen.

2. **Statement 1:** The molality of the solution does not change with temperature

Statement 2: The molality is expressed in units of moles per 1000 g of solvent.

3. **Statement 1:** The percentage of nitrogen in urea is 46.6%.

Statement 2: Urea is a convalent compound.

4. **Statement 1:** H_3PO_3 is a dibasic acid and its salt Na_3PO_3 does not exist.

Statement 2: Being dibasic, only two H's are replaceable.

Integer Answer Type

The answer is a **non-negative integer**.

1. The number of moles and equivalents in 196 g of H_3PO_4 are ________.

2. The number of molecules in 16 g of SO_2 is ________.

3. The number of gram atoms in 24 g of magnesium is ________.

4. The residue obtained on strongly heating 2.48 g Ag_2CO_3 is ________. The reaction is

$$Ag_2CO_3 \xrightarrow{\Delta} Ag + CO_2 + O_2$$

Given that the atomic mass of Ag = 108 u.

5. The atomicity of the molecule of H_2SO_4 is ________.

6. Two moles of 50% pure $Ca(HCO_3)_2$ on heating forms one mole of CO_2. The percentage yield of CO_2 is ________.

7. 4.48 L of ammonia at STP is neutralized using 100 mL of a solution of H_2SO_4, the molarity of acid is ________.

Matrix–Match Type

1. Match the acid with its nature based on its basicity.

Column I	Column II
(A) H_3PO_4	(p) Monobasic
(B) H_3PO_3	(q) Pentabasic
(C) H_3BO_3	(r) Tribasic
(D) EDTA	(s) Tetrabasic
	(t) Dibasic

2. Match the number of moles with their amount.

Column I	Column II
(A) 0.1 mol	(p) 4480 mL of CO_2 at STP
(B) 0.2 mol	(q) 0.1 g atom of iron
(C) 0.25 mol	(r) 1.5×10^{23} molecules of oxygen gas
(D) 0.5 mol	(s) 9 mL of water
	(t) 200 mg of hydrogen gas

3. Match the concentration terms with the factors affecting the concentrations.

Column I	Column II
(A) Molarity (M)	(p) Temperature
(B) Molality (m)	(q) Pressure
(C) Mole fraction (x)	(r) Dilution
(D) Normality	(s) Volume

ANSWERS

Review Questions

2. S.I. signifies International System of Units or *Système Internationale* (in French). The seven basic S.I. units are meter, kilogram, second, ampere, kelvin, mole and candela.

3. Mole is a more convenient unit. Percent mass requires a conversion to moles.

5. **(a)** 1 mol of carbon burns in 1 mol of dioxygen (air) to produce 1 mol of carbon dioxide.
(b) Dioxygen is the limiting reagent.
(c) 16 g of dioxygen can combine with only 0.5 mol of carbon to give 22 g of carbon dioxide.

6. $n + m = p + q$

7. The object is not composed of pure gold.

8. **(a)** centi = 10^{-2}; **(b)** milli = 10^{-3}; **(c)** kilo = 10^{3}; **(d)** micro = 10^{-6}; **(e)** nano = 10^{-9}; **(f)** pico = 10^{-12}; **(g)** mega = 10^{6}.

11. Law of multiple proportions.

13. 6.023×10^{23}

14. False.

15. **(a)** Both contain 1 g atom of carbon that contains 6.023×10^{23} carbon atoms.
(b) 1 mol of H_2O = 18 g

16. Cinnabar is a chemical compound, whereas brass is a mixture.

17. Four.

Numerical Problems

1. 0.74×10^{-10} m;
0.074 nm;
0.74×10^{-4} μm;
0.74×10^{-7} mm

2. 0.35 mol; 0.50 mol

3. $C_{40}H_{56}$

4. $C_{12}H_{26}$

5. **(a)** C_2H_7N; **(b)** C_2H_3N

6. 0.025 M

7. 4 atoms of Fe

8. 1/22.4 mol

9. $M_X = 56$ u, $M_Y = 16$ u

10. 50 g MgO and 10 g O_2

11. 12.78 g of F_2

Additional Objective Questions

Single Correct Choice Type

1. (A)
2. (B)
3. (B)
4. (C)
5. (A)
6. (D)
7. (A)
8. (A)
9. (D)
10. (C)
11. (D)
12. (B)
13. (A)
14. (B)
15. (B)
16. (B)
17. (B)
18. (B)
19. (D)
20. (B)

Multiple Correct Choice Type

1. (A, B)
2. (A, B)
3. (A, D)
4. (A, B, D)

Assertion–Reasoning Type

1. (B)
2. (B)
3. (B)
4. (A)

Integer Answer Type

1. (2, 6)
2. (1.5×10^{23})
3. (1)
4. (2)
5. (7)
6. (100)
7. (1)

Matrix–Match Type

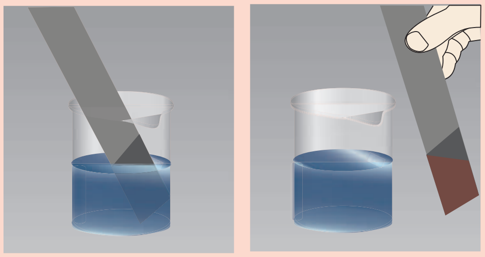
1. A → (r); B → (t); C → (p); D → s)

2. A → (q, t); B → (p); C → (r); D → (s)

3. A → (p, q, r, s); B → (q, r); C → (q, r); D → (r, s)

2

Mole Concept–II



Reaction of zinc with copper ions

Contents

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2.7 Volumetric Analysis
2.8 Types of Titrations
2.9 Applications of Redox Reactions

Among the first reactions studied by early scientists were those that involved oxygen. The combustion of fuels and the reactions of metals with oxygen to give oxides were described by the word *oxidation*. The removal of oxygen from metal oxides to give the metals in their elemental forms was described as *reduction*. In 1789, the French chemist Antoine Lavoisier discovered that *combustion* involves the reaction of chemicals in various fuels, like wood and coal, not just with air but specifically with the oxygen in air. Over time, scientists came to realize that such reactions were actually special cases of a much more general phenomenon, one in which electrons are transferred from one substance to another. Collectively, electron transfer reactions came to be called **oxidation-reduction reactions**, or simply **redox reactions**.

2.1 | OXIDATION NUMBER CONCEPT

Oxidation Number and Oxidation State

The oxidation number of an element indicates the number of electrons lost, gained, or shared when the element changes from free state to form that compound (i.e., as a result of chemical bonding). The change in the oxidation number of a species helps us identify if the element has undergone oxidation or reduction. In a redox reacion, oxidants show a decrease in oxidation number. They have higher oxidation number in a conjugate redox pair. The reductants are substances that show an increase in oxidation number. They have lower oxidation number in the conjugate redox pair. In case of ionic compounds, it represents a real charge while for covalent compounds, it is the charge that atom would have if all electrons in its bonds were assigned to the more electronegative atom. A redox reaction can also be defined as a chemical reaction in which changes in oxidation numbers occur. It is easy to follow redox reactions by taking note of the changes in oxidation numbers. The concept of oxidation number was introduced by chemists to account for electron transfer in redox reactions leading to the formation of covalent compounds. When we assign oxidation numbers to atoms in a compound, the compound is treated as if it were ionic, and the shared electrons in each bond are assigned to the more electronegative element. It does not matter whether the compound actually contains ions. Both the strontium atom in SrF_2 and the carbon atom in CO, for example, are assigned oxidation numbers of +2, even though one of the compounds is predominantly ionic and the other is predominantly covalent.

A term that is frequently used interchangeably with **oxidation number** is **oxidation state**. Oxidation state refers to the degree of oxidation of an atom in a molecule. Each atom of the molecule will have a distinct oxidation state for that molecule where the sum of all the oxidation states will equal the overall electrical charge of the molecule or ion.

Oxidation number is the total charge on all the atoms of the same kind constituting a compound, whereas oxidation state is the charge per atom of all the atoms of the same kind constituting a compound. Thus, oxidation state = oxidation number × total number of atoms of the element in the compound.

In NaCl, sodium has an oxidation number of +1 and is said to be "in the +1 oxidation state". Similarly, the chlorine in NaCl is in the –1 oxidation state. Chemists refer to an atom that has been assigned an oxidation number in a molecule as having a particular **oxidation state**.

There are times when it is convenient to specify the oxidation state of an element when its name is written out. This is done by writing the oxidation number as a Roman numeral in parentheses after the name of the element. For example, "iron(III)" means iron is in the +3 oxidation state. In molecular compounds, the oxidation number is expressed by putting the Roman numeral in parenthesis after the symbol of the metal in the molecular formula. For example, ferric chloride can be represented as $Fe(III)Cl_3$ and ferrous chloride as $Fe(II)Cl_2$. The oxidation number helps in identifying in which compound the element is present in reduced and oxidized states. For example, stannous chloride $Sn(II)Cl_2$ is obtained by the reduction of stannic chloride $Sn(IV)Cl_4$. This notation was given by German Chemist, Alfred Stock and is known as **Stock notation**.

Note: It is assumed that if two or more than two elements of an element are present in a molecule or ion (e.g., two atoms of sulphur in $Na_2S_2O_3$), then the oxidation number of that element is the average of the oxidation number of all the atoms of that element.

Rules for Assigning Oxidation Number

The oxidation number of an element in a particular compound is assigned according to a set of rules, which are described below. For simple, monoatomic ions in a compound such as NaCl, the oxidation numbers are the same as the charges on the ions, so in NaCl the oxidation number of sodium is +1 and the oxidation number of chlorine is –1. However, for molecular compounds, the oxidation number does not actually equal a charge on an atom.

Note: To be sure to differentiate oxidation numbers from actual electrical charges, we will specify the sign *before* the number when writing oxidation numbers, and *after* the number when writing electrical charges. Thus, a sodium ion has a charge of 1+ and an oxidation number of +1.

In covalent compounds, it is not always possible to determine which of the element is more electronegative and hence assign the oxidation number. The following set of rules are followed to determine the oxidation numbers of elements in molecular compounds.

1. The oxidation number of any *free element* (an element not combined chemically with a different element) is zero, regardless of how complex its molecules are. For example, each atom in molecules such as H_2, O_2, S_8, P_4, Ca, K, etc. has oxidation number zero.
2. The oxidation number for any simple, monoatomic ion (e.g., Na^+ or Cl^-) is equal to the charge on the ion. The charge on a polyatomic ion can be viewed as the *net* oxidation number of the ion. The oxidation number of a polyatomic ion is equal to the charge on the ion. For example, the oxidation state of the sulphate ion, (SO_4^{2-}) is –2 and the oxidation state of the phosphate ion, (PO_4^{3-}) is –3.
3. The sum of all the oxidation numbers of the atoms in a molecule or polyatomic ion must equal the charge on the particle. For example, in $Cr_2O_7^{2-}$, the sum of oxidation numbers of two chromium and seven oxygen atoms must be equal to –2. The algebraic sum of oxidation numbers of all the atoms in a compound must be zero.
4. In all its compounds, fluorine has an oxidation number of –1. Other halogens also have –1 oxidation number in their halides but the oxoacids and oxoanions of halogens have positive oxidation numbers.

5. In most of its compounds, hydrogen has an oxidation number of +1. When combined with a less electronegative element (usually a metal), hydrogen has oxidation number –1 (e.g., LiH).
6. In most of its compounds, oxygen has an oxidation number of –2. Exceptions include molecules and polyatomic ions that contain O–O bonds, such as O_2, O_3, H_2O_2 and the O_2^{2-} ion. In peroxide, it is –1, in superoxides, it is –1/2. Oxygen is positive only when bound to the more electronegative fluorine. When it is bonded to fluorine (OF_2 or O_2F_2), the oxidation numbers are +2 and +1, respectively.
7. In binary ionic compounds with metals, the non-metals have oxidation numbers equal to the charges on their anions. For example, Mg_3P contains the phosphide ion P^{3-} which has an oxidation number of –3.

Whenever there is a conflict between two of these rules, *we apply the rule with the lower number and ignore the conflicting rule.*

For example, for determination of oxidation number of atoms in hydrogen peroxide H_2O_2, Rule 6 is the higher numbered rule causing the conflict, so we have to ignore it this time and just apply Rules 3 (the sum rule) and 5 (the rule that tells us the oxidation number of hydrogen is +1). Since we do not have a rule that applies to oxygen in this case, we will represent the oxidation number of O by x.

$$\begin{array}{ll} \text{H}(2\text{ atoms})\times(+1) = +2 & (\text{Rule } 5) \\ \underline{\text{O}(2\text{ atoms})\times(x) \quad = 2x} & \\ \qquad\qquad \text{Sum} = 0 & (\text{Rule } 3) \end{array}$$

For the sum to be zero, $2x = -2$, so $x = -1$. Therefore, in this compound, oxygen has an oxidation number of –1.

Therefore, charge on H = 1+ and that on O = 1–

Similarly for determining the average oxidation number of the nitrogen in sodium azide whose formula is NaN_3, we know that sodium exists as the ion Na^+ and that the compound is neutral overall. Therefore,

$$\begin{array}{ll} \text{Na}(1\text{ atom})\times(+1) = +1 & (\text{Rule } 2) \\ \underline{\text{N}(3\text{ atoms})\times(x) \quad = 3x} & \\ \qquad\qquad \text{Sum} = 0 & (\text{Rule } 3) \end{array}$$

The sum of the oxidation numbers of the three nitrogen atoms in this ion must add up to –1, so each nitrogen must have an oxidation number of –1/3.

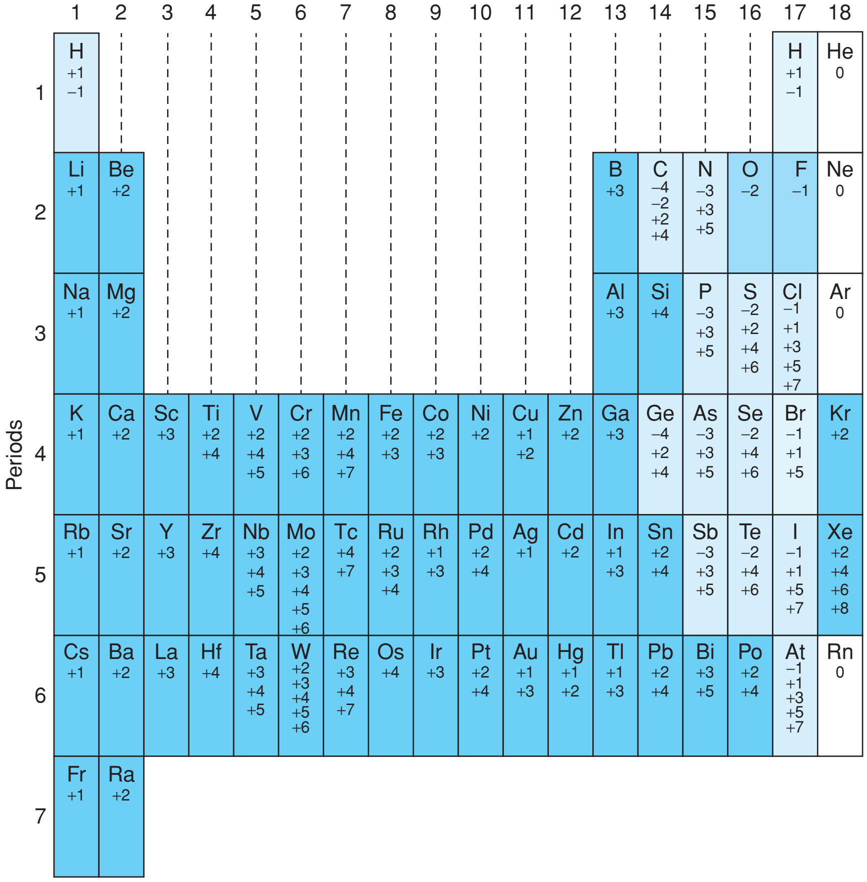
Oxidation Numbers for Different Types of Elements

In addition to these basic rules, some important characteristics of oxidation number of different types of elements are listed as follows: 1. All the metals in Group 1 form ions with a 1+ charge, and all those in Group 2 form ions with a 2+ charge. This means that when we find sodium in a compound, we can assign it an oxidation number of +1 because its simple ion Na^+ has a charge of 1+ (by applying Rule 2). Some elements, particularly transition elements and some *p*-block elements show variable oxidation states. For example, transition element Fe forms Fe^{2+} and Fe^{3+} ions, so in an iron compound we have to use the listed rules to figure out which Fe ion is present. In *p*-block elements, variable oxidation number is shown by As (+3 and +5), Sb (+3 and +5), Sn (+2 and +4), etc.

When non-metals are combined with hydrogen and oxygen in compounds or polyatomic ions, their oxidation number varies and have to be calculated using the above rules. Non-metals can have both positive or negative oxidation numbers.

Figure 2.1 shows the common oxidation numbers for many of the elements in the periodic table. Different shades are used to distinguish among elements that have only positive, only negative, both negative and positive oxidation states. From the figure, the following observations can be made:

1. Elements in the same group often have the same oxidation numbers.
2. The largest, or most positive, oxidation number of an atom is often equal to the group number of the element. For example, the largest oxidation number for phosphorus in Group 15 is +5. (Exceptions are oxygen and fluorine)
3. The smallest, or most negative, oxidation number of a non-metal can often be found by subtracting 8 from the group number. For example, the most negative oxidation state of phosphorus is 5 – 8 = –3.
4. The highest value of oxidation number for the first two groups is the group number while for the rest of the groups, it is group number minus 10.
5. The maximum value of oxidation number of an element increases across the period.
6. Alkali metals have ns^1 configuration and have a tendency to lose this electron. So they show a uniform oxidation state of +1.



Periods	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H +1 −1																H +1 −1	He 0
2	Li +1	Be +2											B +3	C −4 −2 +2 +4	N −3 +3 +5	O −2	F −1	Ne 0
3	Na +1	Mg +2											Al +3	Si +4	P −3 +3 +5	S −2 +2 +4 +6	Cl −1 +1 +3 +5 +7	Ar 0
4	K +1	Ca +2	Sc +3	Ti +2 +4	V +2 +4 +5	Cr +2 +3 +6	Mn +2 +4 +7	Fe +2 +3	Co +2 +3	Ni +2	Cu +1 +2	Zn +2	Ga +3	Ge −4 +2 +4	As −3 +3 +5	Se −2 +4 +6	Br −1 +1 +5	Kr +2
5	Rb +1	Sr +2	Y +3	Zr +4	Nb +3 +4 +5	Mo +2 +3 +4 +5 +6	Tc +4 +7	Ru +2 +3 +4	Rh +1 +3	Pd +2 +4	Ag +1	Cd +2	In +1 +3	Sn +2 +4	Sb −3 +3 +5	Te −2 +4 +6	I −1 +1 +5 +7	Xe +2 +4 +6 +8
6	Cs +1	Ba +2	La +3	Hf +4	Ta +3 +4 +5	W +2 +3 +4 +5 +6	Re +3 +4 +7	Os +4	Ir +3	Pt +2 +4	Au +1 +3	Hg +1 +2	Tl +1 +3	Pb +2 +4	Bi +3 +5	Po +2 +4	At −1 +1 +3 +5 +7	Rn 0
7	Fr +1	Ra +2																

Figure 2.1 Common oxidation numbers of the elements.

7. Alkaline earth metals have ns^2 configuration and show common oxidation state of +2.
8. Elements of Group 13 have outer shell configuration ns^2np^1 and show oxidation state of +1 and +3.
9. Elements of Group 14 have outer shell configuration ns^2np^2 and show maximum oxidation state of +4 and minimum oxidation state of –4. Oxidation state of +2 is also shown by tin and lead and these are metallic in nature.
10. Elements of Group 15 have outer shell configuration ns^2np^3 and show maximum oxidation state of +5 and minimum oxidation state of –3.
11. Elements of Group 16 have outer shell configuration ns^2np^4 and show maximum oxidation state of +6 and minimum oxidation state of –2.
12. Elements of Group 17 have outer shell configuration ns^2np^5 and show maximum oxidation state of +7 and minimum oxidation state of –1.
13. Transition metals can exhibit a large number of oxidation states due to the presence of $(n – 1)d$ electrons along with ns electrons.

Fractional Oxidation Number

The oxidation numbers are usually whole numbers but in certain compounds the calculation of oxidation number yields a fractional number. The element for which fractional oxidation number is observed is present in different oxidation states. For example, let the oxidation number of Fe in Fe_3O_4 be x. The oxygen atom has the oxidation state of –2. Therefore,

$$3x + 4 \times (-2) = 0$$

$$3x = +8x \Rightarrow x = +8/3$$

Fractional oxidation states actually represent the average oxidation states of several atoms in a structure. In most cases, atoms of the same element in a given compound have the same oxidation states, but each atom **can** have a different state than the other. In Fe_3O_4, two Fe atoms have an oxidation number +3 and one has +2, which makes the total oxidation number of Fe = 8/3. The average here, therefore, refers to atoms that are not equivalent but are present in different oxidation states.

Solved Example 2-1

Find oxidation number of Cl in $C_3H_6Cl_2$, Pb in Pb_3O_4 and S in $S_4O_6^{2-}$.

Solution

$C_3H_6Cl_2$: Let the oxidation state of Cl be x, then we have $3(-4) + 6(+1) + 2x = 0$

$-12 + 6 + 2x = 0 \Rightarrow x = +3$.

Pb_3O_4: Let the oxidation state of Pb be x, then we have $3x - 8 = 0 \Rightarrow x = +8/3$.

$S_4O_6^{2-}$: Let the oxidation state of S be x, then we have $4x - 12 = -2 \Rightarrow x = +10/4 = +5/2$.

Solved Example 2-2

Find out the oxidation number of chlorine in the following compounds and arrange them in increasing order of oxidation number of chlorine: $NaClO_4$, $NaClO_3$, NaClO, $NaClO_2$, Cl_2O_7, ClO_3, Cl_2O, NaCl, Cl_2, ClO_2.

Which oxidation state is not present in any of the above compounds?

Solution

Let the oxidation number of chlorine be x. For $NaClO_4$, we have $1 + x + 4(-2) = 0 \Rightarrow x = 7$. Thus oxidation number of chlorine in $NaClO_4$ is +7.

For $NaClO_3$, we have $1 + x + 3(-2) = 0 \Rightarrow x = 5$. Thus oxidation number of chlorine in $NaClO_3$ is +5.

For NaClO, we have $1 + x + (-2) = 0 \Rightarrow x = 1$. Thus oxidation number of chlorine in NaClO is +1.

For $NaClO_2$ we have $1 + x + 2(-2) = 0 \Rightarrow x = 3$. Thus oxidation number of chlorine in $NaClO_2$ is +3.

For Cl_2O_7, we have $2x + 7(-2) = 0 \Rightarrow x = 7$. Thus oxidation number of chlorine in Cl_2O_7 is +7.

For ClO_3, we have $x + 3(-2) = 0 \Rightarrow x = 6$. Thus oxidation number of chlorine in ClO_3 is +6.

For Cl_2O, we have $2x + (-2) = 0 \Rightarrow x = 1$. Thus oxidation number of chlorine in Cl_2O is +1.

For NaCl, we have $1 + x = 0 \Rightarrow x = -1$. Thus oxidation number of chlorine in NaCl is –1.

For Cl_2, we have $2x = 0 \Rightarrow x = 0$. Thus, oxidation number of chlorine in Cl_2 is 0.

For ClO_2, we have $x + 2(-2) = 0 \Rightarrow x = 4$. Thus, oxidation number of chlorine in ClO_2 is +4.

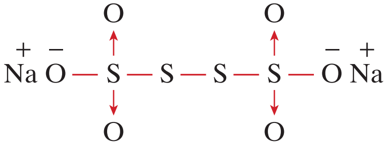
None of the compounds have an oxidation number of +2.

Solved Example 2-3

Determine the oxidation number of sulphur in the following compounds: **(a)** $Na_2S_4O_6$, **(b)** $Na_2S_2O_3$, **(c)** H_2SO_5, **(d)** $H_2S_2O_8$.

Solution

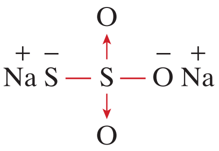
(a) $Na_2S_4O_6$ is represented as



$$\overset{+}{Na}\,\overset{-}{O}-\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}-S-S-\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}-\overset{-}{O}\,\overset{+}{Na}$$

From the structure, it is clear that the sulphur atoms acting as donor atoms have +5 oxidation number (each). However, the sulphur atom involved in pure covalent bond formation has zero oxidation number.

(b) $Na_2S_2O_3$ is represented as



$$\overset{+}{Na}\,\overset{-}{S}-\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}-\overset{-}{O}\,\overset{+}{Na}$$

Suppose average oxidation number of S = x, then we have $+2 + 2x - 6 = 0 \Rightarrow x = +2$.

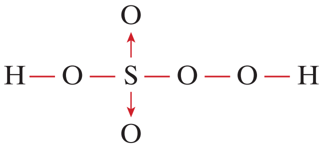
However, here two sulphur atoms have different oxidation states

(i) Sulphur, bonded with Na lies in –1 state since one electron of Na lies towards the sulphur. Electrons of S–S bond are equally shared between two sulphur atoms.

(ii) Oxidation number of donor sulphur atom is +5. It gives up four electrons in coordination and one electron in covalent bond formation with oxygen.

Thus, +5 and –1 are two oxidation states of the two sulphur atoms.

(c) Peroxomonosulphuric acid (H_2SO_5) is represented as



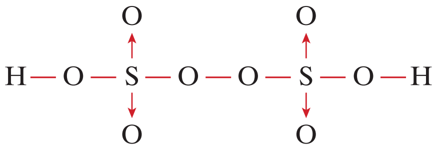
$$H-O-\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}-O-O-H$$

Suppose oxidation number of S = x

Oxidation number of H = +1, oxygen in peroxo linkage = –1, the other oxygen atoms = –2 each.

Therefore, $+2 - 6 + x - 2 = 0 \Rightarrow x = 6$. Thus oxidation number of S = +6.

(d) Perdisulphuric acid ($H_2S_2O_8$) is represented as



$$H-O-\underset{\downarrow\atop O}{\overset{O\atop\uparrow}{S}}-O-O-\underset{\downarrow\atop O}{\overset{O\atop\uparrow}{S}}-O-H$$

Suppose oxidation number of S = x

Oxidation number of H = +1, oxygen in peroxo linkage = –1, the other six oxygen atoms = –2 each

Therefore, $+2 + (-12) + 2x - 2 = 0 \Rightarrow x = 6$. Thus, oxidation number of S = +6.

Solved Example 2-4

Determine the oxidation number of nitrogen in **(a)** NH_2-NH_2, **(b)** NOCl, **(c)** HCN and **(d)** HNC.

Solution

(a) Suppose oxidation number of N = x, then $2x + 4 = 0$ $\Rightarrow x = -2$.

(b) NOCl is represented as $Cl-N{=}O:$. Suppose oxidation number of N = x. The oxidation number of chlorine = –1, oxygen = –2. Thus, $-1 + x - 2 = 0 \Rightarrow x = +3$.

(c) In HCN, nitrogen is more electronegative than carbon, so each covalent bond gives an oxidation number of –1 to nitrogen. There are three covalent bonds, therefore, in HCN, the oxidation of N = –3.

(d) In HNC, N is more electronegative than C, so contribution of coordinate bond is neglected, thus oxidation number of N remains –3 since it has three covalent bonds.

Solved Example 2-5

Determine the oxidation number of carbon in **(a)** C_3O_2, **(b)** HCN and **(c)** HNC.

Solution

(a) Since, oxygen is more electronegative than carbon, carbon has positive oxidation state in C_3O_2

$$\overset{-2}{O}=\overset{+2}{C}=\overset{0}{C}=\overset{+2}{C}=\overset{-2}{O}$$

Average oxidation state = +4/3

(b) Suppose oxidation state of C = x. In HCN, nitrogen is more electronegative than carbon, so each covalent bond gives an oxidation number of –1 to nitrogen. There are three covalent bonds, therefore, in HCN, the oxidation of N = –3. Therefore, $+1 + x - 3 = 0 \Rightarrow x = +2$.

(b) Suppose oxidation state of C = x. In HNC, N is more electronegative than C, so contribution of coordinate bond is neglected, thus oxidation number of N remains –3 since it has three covalent bonds. Therefore, $+1 + x - 3 = 0 \Rightarrow x = +2$.

Solved Example 2-6

In the following unbalanced equations, indicate the reactant oxidized, the reactant reduced, the oxidizing agent and the reducing agent. Indicate the products that contain the elements that were oxidized or reduced.

(a) $Al + HCl \rightarrow AlCl_3 + H_2$

(b) $CH_4 + O_2 \rightarrow CO_2 + H_2O$

(c) $MnO_2 + HCl \rightarrow MnCl_2 + Cl_2 + H_2O$

(d) $K_2Cr_2O_7 + SnCl_2 + HCl \rightarrow CrCl_3 + SnCl_4 + KCl + H_2O$

Solution

(a) Oxidation states of elements:

$$\overset{0}{Al} + \overset{+1\ -1}{HCl} \rightarrow \overset{+3\ -1}{AlCl_3} + \overset{0}{H_2}$$

Reactant	Change	Agent	Product
Al	Oxidized	Reducing	$AlCl_3$
HCl	Reduced	Oxidizing	H_2

(b) Oxidation states of elements:

$$\overset{-4\ +1}{CH_4} + \overset{0}{O_2} \rightarrow \overset{+4\ -2}{CO_2} \rightarrow \overset{+1\ -2}{H_2O}$$

Reactant	Change	Agent	Product
CH_4	Oxidized	Reducing	CO_2
O_2	Reduced	Oxidizing	CO_2, H_2O

(c) Oxidation states of elements:

$$\overset{+4\ -2}{MnO_2} + \overset{+1\ -1}{HCl} \rightarrow \overset{+2\ -1}{MnCl_2} + \overset{0}{Cl_2} + \overset{+1\ -2}{H_2O}$$

Reactant	Change	Agent	Product
HCl	Oxidized	reducing	Cl_2
MnO_2	Reduced	oxidizing	$MnCl_2$

Reactant	Change	Agent	Product
$SnCl_2$	Oxidized	reducing	$SnCl_4$
$K_2Cr_2O_7$	Reduced	oxidizing	$CrCl_3$

(d) Oxidation states of elements:

$$\overset{+1}{K_2}\overset{+6}{Cr_2}\overset{-2}{O_7}+\overset{+2}{Sn}\overset{-1}{Cl_2}+\overset{+1}{H}\overset{-1}{Cl}\rightarrow \overset{+3}{Cr}\overset{-1}{Cl_3}+\overset{+1}{K}\overset{-1}{Cl}+\overset{+4}{Sn}\overset{-1}{Cl_4}+\overset{+1}{H_2}\overset{-2}{O}$$

Solved Example 2-7

Is the following a redox reaction? If so, identify the substance oxidized and the substance reduced as well as the oxidizing and reducing agents.

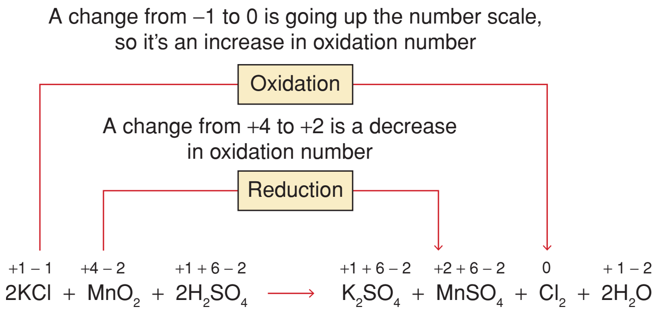
$$2KCl+MnO_2+2H_2SO_4\rightarrow K_2SO_4+MnSO_4+Cl_2+2H_2O$$

Solution

To determine whether redox reaction is occurring here, we first must assign oxidation numbers to each atom on both sides of the equation. Following the rules, we get

$$2\overset{+1}{K}\overset{-1}{Cl}+\overset{+4}{Mn}\overset{-2}{O_2}+2\overset{+1}{H_2}\overset{+6}{S}\overset{-2}{O_4}\rightarrow \overset{+1}{K_2}\overset{+6}{S}\overset{-2}{O_4}+\overset{+2}{Mn}\overset{+6}{S}\overset{-2}{O_4}+\overset{0}{Cl_2}+2\overset{+1}{H_2}\overset{-2}{O}$$

Next we look for changes, keeping in mind that an increase in oxidation number is oxidation and a decrease is reduction.


A change from –1 to 0 is going up the number scale, so it's an increase in oxidation number
Oxidation
A change from +4 to +2 is a decrease in oxidation number
Reduction
+1 –1 +4 –2 +1 +6 –2 +1 +6 –2 +2 +6 –2 0 +1 –2
2KCl + MnO2 + 2H2SO4 ⟶ K2SO4 + MnSO4 + Cl2 + 2H2O

Thus, the Cl in KCl is oxidized and the Mn in MnO_2 is reduced. The reducing agent is KCl and the oxidizing agent is MnO_2. (Notice that when we identify the oxidizing and reducing agents, we give the entire formulas for the substances that contain the atoms with oxidation numbers that change.)

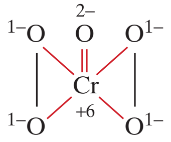
Solved Example 2-8

Determine the oxidation state of chlorine in $CaOCl_2$ and chromium in CrO_5.

Solution

Based oxidation state of Ca atom as +2 and that of O atom as –2, we can calculate the oxidation state (x) of Cl atom as $2x + 2 - 2 = 0 \Rightarrow x = 0$. Based on stoichiometry of the compound, where composition of $CaOCl_2$ is $Ca^{2+}(OCl^-)Cl^-$, we see that oxidation state of Cl in $Ca^+(OCl^-)$ is +1 and that in Cl^- is –1.

The structure of CrO_5 is



It can be seen that four of the oxygen atoms are linked through peroxide linkage, while one oxygen atom is double bonded to Cr. So, the oxidation state of Cr can be found as

$$x+4(-1)-2=0\Rightarrow x=+6$$

Solved Example 2-9

When hydrogen peroxide is used as an antiseptic, it kills bacteria by oxidizing them. When the H_2O_2 serves as an oxidizing agent, which product might be formed from it, O_2 or H_2O? Why?

Solution

If H_2O_2 acts as an oxidizing agent, it gets reduced itself in the process. Examining the oxidation numbers, we have

$$\overset{+1}{H_2}\overset{-1}{O_2}\rightarrow \overset{+1}{H_2}\overset{-2}{O}+\overset{0}{O_2}$$

If H_2O_2 is reduced it must form water, since the oxidation number of oxygen drops from –1 to –2 in the formation of water (a reduction). The product is, therefore, water.

Oxidation Number and Valency

The electrons in the outermost shell/orbit of an atom are called valence electrons. These electrons can be accepted or shared by an atom of any element. In some cases, the valency and oxidation number are the same like in case of electrovalent compounds. The differences between the two are as follows:

1. Oxidation number is the charge present on that atom if all electrons in its bonds were assigned to the more electronegative atom, whereas valency is the number of electrons which can be accepted or lost while combining with other elements.
2. Oxidation number has a positive or negative sign, and can be whole number or fractional, whereas valency does not have any positive or negative sign, and can never be fractional.
3. Oxidation number can be zero for any element, whereas valency can be zero only for noble gases.

Limitations of Concept of Oxidation Number

The definitions of oxidation and reduction are under constant change depending on the new discoveries and insights into the redox processes. Apart from transfer of electrons, the reactions are now viewed in terms of electron densities wherein, oxidation involves decrease in electron density while reduction involves an increase in it.

Solved Example 2-10

Indicate valency and oxidation number of carbon in the following compounds: CH_4, CH_3Cl, CH_2Cl_2, $CHCl_3$, CCl_4.

Solution

For methane CH_4, valency of carbon is 4 and oxidation state is –4.

For methyl chloride CH_3Cl, valency of carbon is 4 and oxidation state is –2.

For CH_2Cl_2, valency of carbon is 4 and oxidation state is 0.

For $CHCl_3$, valency of carbon is 4 and oxidation state is +2.

For CCl_4, valency of carbon is 4 and oxidation state is +4.

Solved Example 2-11

A polyvalent metal weighting 0.1 g and having atomic weight of 50 reacted with dilute H_2SO_4 to give 44.8 mL of hydrogen at STP. The solution containing the metal in this lower oxidation state, was found to require 60 mL of 0.1 N $KMnO_4$ solution for complete oxidation. What are valencies of metal?

Solution

The reaction involved is $\text{Metal(M)} + H_2SO_4 \rightarrow H_2$

44.8 mL H_2 at STP $\equiv \dfrac{44.8}{22400}$ mol of H_2

Now, milliequiv. of M = milliequiv. of H_2O

For hydrogen, the reaction is

$$2H^+ + 2e^- \rightarrow H_2$$

Milliequiv. of $H_2 = 2 \times$ moles of H_2

or
$$\frac{0.1}{50/x} = \left(\frac{44.8}{2200}\right) \times 2 \Rightarrow x = 2$$

Thus, in the reaction $M - xe^- \rightarrow Mx^+$, $x = 2$ or oxidation state is + 2.

Now M^{2+} will acquire higher oxidation state when oxidized by $KMnO_4$

$$M^{2+} - ne^- \rightarrow M^{2+n}$$

Now, milliequiv. of M^{2+} = milliequiv. of $KMnO_4$

$$\frac{0.1}{50/n} \times 1000 = 0.1 \times 60 \Rightarrow n = 2$$

So oxidation state of M is $M^{2+n} \equiv M^{+5}$. Hence, the possible valencies of the metal are +2 and +5.

Types of Redox Reactions

1. **Combination reactions:** These reactions involve combining of two or more reactants to form a single product. It can be represented by a reaction of the type,

$$A + B \rightarrow AB$$

For a redox reaction, either A or B or both must be in the elemental form. The combustion reactions of fuels are generally combination reactions of carbon and hydrocarbons with elemental dioxygen.

$$\overset{0}{C}(s)+\overset{0}{O}_2(g)\xrightarrow{\Delta}\overset{+4}{C}\overset{-2}{O}_2(g)$$

$$CH_4(g)+2O_2(g)\rightarrow CO_2(g)+2H_2O(l)$$

$$2C_8H_{18}(s)+25O_2(g)\rightarrow 16CO_2(g)+18H_2O(l)$$

Combustion of magnesium metal with dioxygen or lithium with nitrogen are also examples of combination redox reactions.

$$2Mg(s)+\overset{0}{O}_2(g)\rightarrow \overset{+2}{Mg}\overset{-2}{O}(s)$$

$$3\overset{0}{Li}(s)+\tfrac{1}{2}\overset{0}{N}_2(g)\rightarrow \overset{+1}{Li}_3\overset{-3}{N}(s)$$

2. **Decomposition reactions:** These reactions are reverse of combination reactions and involve breakdown of a reactants into two or more products.

$$AB\rightarrow A+B$$

For these reactions to be redox, at least one of the components formed should be in the elemental state. For example, the decomposition of potassium chlorate or hydrogen peroxide is a redox reaction, whereas the decomposition of calcium carbonate or other metal carbonates is not a redox reaction because none of the components formed are in the elemental state.

$$2\overset{+1}{K}\overset{+5}{Cl}\overset{-2}{O}_3(s)\xrightarrow{\Delta}2\overset{+1}{K}\overset{-1}{Cl}(s)+3\overset{0}{O}_2(g)$$

$$2\overset{+1}{H}_2\overset{-2}{O}_2(l)\xrightarrow{\Delta}2\overset{0}{H}_2(g)+\overset{0}{O}_2(g)$$

$$\overset{+2}{Ca}\overset{+4}{C}\overset{-2}{O}_3(s)\xrightarrow{\Delta}\overset{+2}{Ca}\overset{-2}{O}(s)+\overset{+4}{C}\overset{-2}{O}_2(g)$$

3. **Displacement reactions:** These reactions are redox reactions in which one element of the compound is replaced by atom or ion of another element. It can be represented as

$$AB+C\rightarrow AC+B$$

The necessary condition for the reaction is that C is more reactive than B. Since B and C are in their elemental state, the reaction is a redox reaction, where the main step involves the movement of electrons from one reactant to another. Displacement reactions can be further classified on the basis of nature of displacing element, into metal and non-metal displacements.

(a) **Metal displacement:** If one metal is more easily oxidized than another, it can displace the other metal from its compounds by a redox reaction. Such a reaction can be represented as

$$AX+M\rightarrow MX+A$$

These reactions are also called single displacement reactions. The atoms of more active metals are oxidized and become ions whereas the ions of less active metals are reduced and become atoms. Some examples are

$$Cu(s)+2AgNO_3(aq)\rightarrow 2Ag(s)+Cu(NO_3)_2(aq)$$

$$Zn(s)+HgO(s)\rightarrow ZnO(s)+Hg(l)$$

$$Cr_2O_3(s)+Al(s)\rightarrow Al_2O_3(s)+Cr(s)$$

$$2Cr(s)+3Cu(NO_3)_2(aq)\rightarrow 3Cu(s)+2Cr(NO_3)_3(aq)$$

(b) **Non-metal displacement:** The non-metal displacement reactions involve displacement of hydrogen and in some cases oxygen. The hydrogen displacement reactions are listed as follow.

- **Metals replacing hydrogen from cold water:** All alkali and some alkaline earth metals, such as Ca, Sr and Ba, displace hydrogen from cold water and are strong reducing agents.

$$2K(s)+2H_2O(l)\rightarrow 2KOH(aq)+H_2(g)$$

$$Ba(s)+2H_2O(l)\rightarrow Ba(OH)_2(aq)+H_2(g)$$

The hydrogen displaced from water has electropositive character. In the above reactions, the more electropositive K^+ and Ba^+ displace the less positive hydrogen.

- **Metals replacing hydrogen from steam:** Less reactive metals such as iron displaces hydrogen from steam to give hydrogen gas.

  $$2Fe(s) + 3H_2O\ (steam) \rightarrow 2Fe_2O_3(s) + 3H_2(g)$$

  Similarly, reaction between red-hot iron and superheated steam gives hydrogen gas:

  $$3Fe(s) + 4H_2O(steam) \rightarrow Fe_3O_4(s) + 4H_2(g)$$

- **Metals replacing hydrogen from acid:** Metals that do not react with cold water can displace hydrogen from acids. The reaction is also shown by metals that do not react even with steam. For example, when a piece of zinc is placed into a solution of hydrochloric acid, bubbling is observed and the zinc gradually dissolves. The chemical reaction is

  $$Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$$

  Similarly,

  $$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$$

  $$Sn(s) + 2HCl(aq) \rightarrow SnCl_2(aq) + H_2(g)$$

  The rate of reaction is fast with zinc or magnesium and the reaction is used as a method for preparation of hydrogen in the laboratory. The rate of evolution of hydrogen gas is a measure of the reactivity of the metals. Magnesium is the most reactive metal and iron the least reactive in displacement of hydrogen from an acid. Metals which occur in their native state, such as gold and silver do not react with acids to liberate hydrogen.

Like metals, halogens can also be arranged in activity series based on their reactivity as oxidizing agents. Their strength as oxidizing agents decreases as we move down the group from fluorine to iodine. Fluorine is the most reactive and can displace oxygen from water.

$$2\overset{0}{F_2}(g) + 2\overset{+1}{H_2}\overset{-2}{O}(l) \rightarrow 4\overset{+1}{H}\overset{-1}{F}(aq) + \overset{0}{O_2}(g)$$

The displacement reactions of chlorine, bromine and iodine using fluorine are not carried out in aqueous medium because of fluorine's ability to displace oxygen from water. However, chlorine can displace bromine and iodine in aqueous solutions and bromine can displace iodine.

$$Cl_2(g) + 2NaBr(aq) \rightarrow 2NaCl(aq) + Br_2(l)$$
$$Cl_2(g) + 2NaI(aq) \rightarrow 2NaCl(aq) + I_2(s)$$
$$Br_2(l) + 2NaI(aq) \rightarrow 2NaBr(aq) + I_2(s)$$

Note: Both bromine and iodine dissolve in CCl_4 and impart reddish brown and violet color to the solution, respectively. These displacement reactions form the basis of the **layer test** used in the laboratory for identification of bromide and iodide ions.

4. **Disproportionation reactions:** These reactions are redox reactions in which an element in a compound is simultaneously oxidized as well as reduced. In the reactant, the element is in one oxidation state while in the products it appears in more than one oxidation state, one reflecting oxidation and the other reduction.

Note: The essential condition for this type of redox reaction is that an element in the reactant should be able to exist in at least three oxidation states and in the reactant it should be in the intermediate oxidation state.

Consider the example of reaction of chlorine gas with sodium hydroxide to form sodium chloride, sodium hypochlorite and water. In the reactant, the elemental chlorine has oxidation state zero and in the products oxidation state of chlorine in sodium chloride is –1 (reduction) and in sodium chlorate it is +1 (oxidation).

$$\overset{0}{Cl_2}(g) + 2\overset{+1}{Na}\overset{-2}{O}\overset{+1}{H}(aq) \rightarrow \overset{+1}{Na}\overset{-1}{Cl}(aq) + \overset{+1}{Na}\overset{+1}{Cl}\overset{-2}{O}(aq) + \overset{+1}{H_2}\overset{-2}{O}(l)$$

The halogens bromine and iodine also exhibit the same reaction on treatment with alkali. However, the reaction of fluorine with alkali shows a deviation and the reaction proceeds as follows:

$$2F_2(g) + 2NaOH(aq) \rightarrow 2NaF + OF_2(g) + H_2O(l)$$

This behavior of fluorine is attributed to the fact that it is the most electronegative element and can exhibit only the –1 oxidation state in all its compounds. Hence, the tendency to undergo disproportionation redox reactions is not possible in the case of fluorine. Phosphorus and sulphur also undergo disproportionation reactions in alkaline medium.

$$\overset{0}{P}_4(s) + 3NaOH(aq) + 3H_2O(l) \rightarrow \overset{-3}{P}H_3(g) + 3NaH_2\overset{+1}{P}O_2$$
$$\overset{0}{S}_8(s) + 12NaOH(aq) \rightarrow 4Na_2\overset{2-}{S}(aq) + 2Na_2\overset{2+}{S}_2O_3(aq) + 6H_2O(l)$$

The reaction of Pb_3O_4 proceeds differently with acids HCl and HNO_3.

$$Pb_3O_4 + 8HCl \rightarrow 3PbCl_2 + Cl_2 + 4H_2O$$
$$Pb_3O_4 + 4HNO_3 \rightarrow 2Pb(NO_3)_2 + PbO_2 + 2H_2O$$

This can be explained on the basis of the fact that the oxide is a mixture of two oxides

$$Pb_3O_4 \Leftrightarrow PbO\ (2\ mol) + PbO_2\ (1\ mol) \Leftrightarrow 2PbO \cdot PbO_2$$

The difference arises due to difference in reaction of these two oxides constituting Pb_3O_4 with the two acids. Reaction with HCl proceeds as follows

$$2PbO + 4HCl \rightarrow 2PbCl_2 + 2H_2O \qquad \text{(Acid – base reaction)}$$
$$PbO_2 + 4HCl \rightarrow PbCl_2 + Cl_2 + H_2O \qquad \text{(Redox reaction)}$$

In case of reaction with HNO_3, no redox reaction takes place between PbO_2 and HNO_3 as nitric acid itself is an oxidizing agent. Only the acid–base reaction takes place and PbO_2 is reflected in the products.

$$2PbO + 4HNO_3 \rightarrow 2Pb(NO_3)_2 + 2H_2O \qquad \text{(Acid – base reaction)}$$

Solved Example 2-12

Classify the following reactions by type and assign the oxidation number to the elements.

(a) $2FeCl_2 + Cl_2 \rightarrow 2FeCl_3$

(b) $2NO_2 + H_2O \rightarrow HNO_2 + HNO_3$

(c) $Mg + 2AgNO_3 \rightarrow Mg(NO_3)_2 + 2Ag$

Solution

(a) This is a combination reaction, where two reactants combine to form a single product. The oxidation number of Fe changes from +2 to +3 and that of Cl changes from 0 to –1.

(b) This is a disproportionation reaction. The oxidation number of the elements on both sides of the equation is the same. N is +4 in NO_2 (2 mol) and in the product side it is +3 in HNO_2 and +5 in HNO_3.

(c) This is a metal displacement reaction in which Mg replaces Ag. The oxidation number of Mg changes from 0 to +2 and Ag is reduced from +1 to 0.

Solved Example 2-13

Classify the following redox reactions by type and assign oxidation number to the elements:

(a) $NH_4NO_2 \rightarrow N_2 + H_2O$

(b) $Ba(NO_3)_2 + Na_2SO_4 \rightarrow 2NaNO_3 + BaSO_4$

(c) $P_4 + 10Cl_2 \rightarrow 4PCl_5$

(d) $3HNO_2 \rightarrow HNO_3 + H_2O + 2NO$

Solution

(a) $\overset{-3}{N}\overset{+1}{H}_4\overset{+3}{N}\overset{-2}{O}_2 \rightarrow \overset{0}{N}_2 + \overset{+}{H}_2\overset{-2}{O}$ Decomposition

(b) $\overset{+4}{Ba}(\overset{+4}{N}\overset{-2}{O}_3)_2 + \overset{+1}{Na}_2\overset{+6}{S}\overset{-2}{O}_4 \rightarrow 2\overset{+1}{Na}\overset{+5}{N}\overset{-2}{O}_3 + \overset{+2}{Ba}\overset{+6}{S}\overset{-2}{O}_4$
Metal displacement

(c) $\overset{0}{P}_4 + 10\overset{0}{Cl}_2 \rightarrow 4\overset{+5}{P}\overset{-1}{Cl}_5$ Combination

(d) $3\overset{+1}{H}\overset{+3}{N}\overset{-2}{O}_2 \rightarrow \overset{+1}{H}\overset{+5}{N}\overset{-2}{O}_3 + \overset{+1}{H}_2\overset{-2}{O} + 2\overset{+2}{N}\overset{-2}{O}$
Disproportionation

Solved Example 2-14

Identify the type of redox reaction taking place in the following and indicate the oxidation states of each atom.

(a) $3Mg(s) + N_2(g) \xrightarrow{\Delta} Mg_3N_2(s)$

(b) $V_2O_5(s) + 5Ca(s) \xrightarrow{\Delta} 2V(s) + 5CaO(s)$

(c) $2KClO_3(s) \xrightarrow{\Delta} 2KCl(s) + 3O_2(g)$

(d) $Ca(s) + 2H_2O(l) \rightarrow Ca(OH)_2(aq) + H_2(g)$

(e) $Br_2(l) + 2I^-(aq) \rightarrow 2Br^-(aq) + I_2(s)$

(f) $Cl_2(g) + 2OH^-(aq) \rightarrow ClO^-(aq) + Cl^-(aq) + H_2O(l)$

Solution

(a) $3\overset{0}{Mg}(s) + \overset{0}{N_2}(g) \xrightarrow{\Delta} \overset{+2}{Mg_3}\overset{-3}{N_2}(s)$

Combination reaction

(b) $\overset{+5}{V_2}\overset{-2}{O_5}(s) + 5\overset{0}{Ca}(s) \xrightarrow{\Delta} 2\overset{0}{V}(s) + 5\overset{+2}{Ca}\overset{-2}{O}(s)$

Displacement reaction

(c) $2\overset{+1}{k}\overset{+5}{Cl}\overset{-2}{O_3}(s) \xrightarrow{\Delta} 2\overset{+1}{K}\overset{-1}{Cl}(s) + 3\overset{0}{O_2}(g)$

Decomposition reaction

(d) $\overset{0}{Ca}(s) + 2\overset{+1}{H_2}\overset{-2}{O}(l) \rightarrow \overset{+2}{Ca}(\overset{-2}{O}\overset{+1}{H})_2(aq) + \overset{0}{H_2}(g)$

Metal displacement reaction

(e) $\overset{0}{Br_2}(1) + 2\overset{-1}{I^-}(aq) \rightarrow 2\overset{-1}{Br^-}(aq) + I_2(s)$

Non-metal displacement reaction

(f) $\overset{0}{Cl_2}(g) + 2OH^-(aq) \rightarrow \overset{+1}{Cl}O^-(aq) + \overset{-1}{Cl^-}(aq) + H_2O(l)$

Disproportionation reaction

2.2 | OXIDATION AND REDUCTION

Oxidation is defined as *addition of oxygen or electronegative element to a substance or removal of hydrogen/electropositive element from a substance*.

Some examples of oxidation that are in accordance with the above definition of oxidation are as follows:

1. **Addition of oxygen:** Most metals react directly with oxygen, for example burning of magnesium ribbon in air, and the reaction of addition of oxygen is called oxidation. The reaction generally causes the surface of metal to tarnish because the oxidation products dull the shiny metal surface. For example, iron is oxidized fairly easily, especially in the presence of moisture and forms rust which is a form of iron(III) oxide. A freshly exposed aluminium surface is also easily oxidized on reaction with oxygen and becomes coated with a very thin film of aluminium oxide, Al_2O_3.

   Most non-metals combine as readily with oxygen as do the metals, and their reactions usually occur rapidly enough to be described as combustion. Sulphur burns readily in oxygen to form sulphur dioxide and this is the first step in the manufacture of sulphuric acid.

   $$S(s) + O_2(g) \rightarrow SO_2(g)$$

2. **Removal of hydrogen:** Natural gas is composed principally of methane, CH_4. When hydrocarbons burn in a plentiful supply of oxygen, the products of combustion are always carbon dioxide and water. Thus, methane reacts with oxygen according to the equation.

   $$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$
   $$H_2S + Cl_2 \rightarrow 2HCl + S$$

   In the reactions, the hydrogen of methane thus gets replaced by oxygen, and hydrogen sulphide is oxidized to elemental sulphur by removal of hydrogen. Thus, definition of oxidation can be broadened to include removal of hydrogen.

3. **Addition of electronegative element:** The scope of oxidation reaction was extended further to include reactions not only with oxygen but with other electronegative elements. For example, sodium reacts with chlorine to form NaCl as follows:

   $$2Na + Cl_2 \rightarrow 2NaCl$$

   This reaction did not involve addition of oxygen or removal of hydrogen but is an oxidation reaction. The scope of oxidation thus also extends to removal of electropositive elements.

Similarly, in the following reaction, $SnCl_2$ is oxidized to $SnCl_4$ as two electronegative chlorine atoms are added.

$$2FeCl_3 + SnCl_2 \rightarrow 2FeCl_2 + SnCl_4$$

4. **Removal of electropositive element:** In the following reaction, potassium, an electropositive element, is removed from potassium ferrocyanide and it changes to potassium ferricyanide.

$$2K_4[Fe(CN)_6] + Cl_2 \rightarrow 2K_3[Fe(CN)_6] + 2KCl$$

Similarly, KI is oxidized when electropositive potassium atom is removed and iodine is liberated.

$$2KI + Cl_2 \rightarrow 2KCl + I_2$$

The term *reduction* comes from the Latin meaning "to lead back." Anything that leads back to magnesium metal therefore involves reduction. The reaction between magnesium oxide and carbon at 2000°C to form magnesium metal and carbon monoxide is an example of the reduction of magnesium oxide to magnesium metal.

$$Mg\underbrace{O(s) + C(s) \rightarrow Mg}_{\text{Reduction}}(s) + CO(g)$$

Reduction is defined as *removal of oxygen/electronegative element from a substance or addition of hydrogen/electropositive element to a substance*.

Some examples of reduction that are in accordance with the above definition of reduction are as follows:

1. **Removal of oxygen:**

$$CuO + H_2 \rightarrow Cu + H_2O$$

$$2HgO(s) \xrightarrow{\Delta} 2Hg\,(l) + O_2(g)$$

2. **Removal of electronegative element:**

$$2FeCl_3(aq) + H_2(g) \rightarrow 2FeCl_2(aq) + 2HCl(aq)$$

The above reaction takes place only with nascent hydrogen (that is, hydrogen in the atomic state and not molecular hydrogen). Therefore, the reaction should be written as

$$2FeCl_3(aq) + 2[H](g) \rightarrow 2FeCl_2(aq) + 2HCl(aq)$$

$$2FeCl_3 + SnCl_2 \rightarrow 2FeCl_2 + SnCl_4$$

3. **Addition of hydrogen:**

$$C_2H_4(g) + H_2(g) \rightleftharpoons C_2H_6(g)$$

4. **Addition of electropositive element:**

$$Na + \tfrac{1}{2}Cl_2 \rightarrow NaCl$$

$$2HgCl_2(aq) + SnCl_2(aq) \rightarrow Hg_2Cl_2(s) + SnCl_4(aq)$$

Oxidation and reduction always occur together, that is, no substance is ever oxidized unless something else is reduced. Therefore, these reactions are collectively called **oxidation–reduction** or **redox** reactions.

For example, consider the following reactions.

$$2FeCl_3 + SnCl_2 \rightarrow 2FeCl_2 + SnCl_4$$

$$2HgCl_2(aq) + SnCl_2(aq) \rightarrow Hg_2Cl_2(s) + SnCl_4(aq)$$

In the first reaction, $FeCl_3$ undergoes reduction due to removal of electronegative atom chlorine and $SnCl_2$ is simultaneously oxidized due to addition of electronegative atom chlorine. In the second reaction, $HgCl_2$ is reduced due to addition of electropositive atom Hg, and $SnCl_2$ is oxidized due to addition of electronegative atom chlorine.

Solved Example 2-15

1. Which of the following reactions are oxidation–reduction reactions? Which species is undergoing oxidation, and which is undergoing reduction?
   - **(a)** $2H_2 + O_2 \to 2H_2O$
   - **(b)** $CaCO_3 \to CaO + CO_2$
   - **(c)** $2Na + 2H_2O \to 2NaOH + H_2$
   - **(d)** $2HNO_3 + Ca(OH)_2 \to Ca(NO_3)_2 + 2H_2O$
   - **(e)** $AgNO_3 + KCl \to AgCl + KNO_3$
   - **(f)** $Zn + CuCl_2 \to ZnCl_2 + Cu$

Solution

(a) In the reaction $2H_2 + O_2 \to 2H_2O$, H_2 is oxidized due to addition of oxygen and O_2 is reduced.

(c) In the reaction $2Na + 2H_2O \to 2NaOH + H_2$, Na is oxidized due to addition of oxygen, and H_2O is reduced due to removal of oxygen.

(f) In the reaction $Zn + CuCl_2 \to ZnCl_2 + Cu$, Zn is oxidized due to addition of electronegative group (Cl^-), and $CuCl_2$ is reduced due to removal of electronegative group.

The rest of the reactions **(b)** is a decomposition reaction, while **(d)** and **(e)** are exchange reactions.

Oxidation and Reduction as Electron Transfer Reactions

It was later realized that redox reactions were actually special cases in which electrons are transferred from one substance to another. Thus, electron transfer reactions became known as oxidation–reduction reactions, or simply redox reactions.

1. **Oxidation** is a process in which one or more electrons are lost by one reactant and the valency of the element increases.

2. **Reduction** is a process in which one or more electrons are gained by another reactant and the valency of the element decreases.

Any oxidation–reduction reaction can be split into two or more parts known as **half reactions** to separately highlight the oxidation step and the reduction step.

For example, sodium reacts with chlorine to form sodium chloride as already discussed. This reaction involves a loss of electrons by sodium (**oxidation** of sodium) and a gain of electrons by chlorine (**reduction** of chlorine).

$$Na \to Na^+ + e^- \quad \text{(oxidation)}$$
$$Cl_2 + 2e^- \to 2Cl^- \quad \text{(reduction)}$$

where electrons are represented by the symbol e^-. The electron appears as a "product" if the process is oxidation and as a "reactant" if the process is reduction.

The overall reaction then becomes:

$$2Na(s) + Cl_2(g) \to 2Na^+Cl^-(s)$$

The total number of electrons lost by one substance is always the same as the total number gained by the other. If this were not true, electrons would appear as a product of the overall reaction, and this is never observed. When two sodium atoms are oxidized, two electrons are lost, which is exactly the number of electrons gained when one Cl_2 molecule is reduced.

Some other examples of redox reactions are given in Table 2.1.

Table 2.1 Examples of redox reactions

Reaction	Half-reactions	Explanation
$Mg(s) + Cl_2(g) \rightarrow MgCl_2\ (aq)$ $2Mg(s) + O_2(g) \rightarrow 2MgO(s)$	$Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$ $Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$ $Mg(s) \rightarrow Mg^{2+}(s) + 2e^-$ $O_2(g) + 2e^- \rightarrow O^{2-}(s)$	Magnesium is oxidized due to addition of oxygen or electronegative element chlorine. On the other hand, chlorine and oxygen are reduced due to addition of electropositive element magnesium. These compounds are ionic in nature and can be written as $Mg^{2+}(Cl^-)_2$ and $Mg^{2+}O^{2-}$. So, effectively magnesium loses two electrons to form Mg^{2+} while chlorine gains two electrons to form $(Cl^-)_2$ and oxygen to form O^{2-}.
$2FeCl_3(aq) + SnCl_2(s) \rightarrow 2FeCl_2(s) + SnCl_4(aq)$	$2Fe^{3+}(aq) + 2e^- \rightarrow 2Fe^{2+}(aq)$ $Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2e^-$	The Cl^- ions do not take part in the reaction and remain unchanged. They are often called "**spectator ions**". Therefore, we may cancel $8Cl^-$ on both sides and rewrite the equation as $2Fe^{3+} + Sn^{2+} \rightarrow 2Fe^{2+} + Sn^{4+}$
$Cu(s) + 2AgNH_3(aq) \rightarrow Cu(NH_3)_2(aq) + 2Ag(s)$	$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$ $2Ag^+(aq) + 2e^- \rightarrow 2Ag(s)$	Copper wire is placed in an aqueous solution of the Ag^+ ion. Silver ions are reduced to silver metal to produce whiskers of silver metal that grow out from the copper wire and copper is oxidized to copper ions that impart bluish green color to the solution. The reaction involves the net transfer of electrons from copper metal to Ag^+ ions. $Cu(s) + 2Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$ The presence of copper ions can be confirmed by adding ammonia to this solution to form the deep blue $Cu(NH_3)_4^{2+}$ complex ion.

Since electrons are neither created nor destroyed in a chemical reaction, oxidation and reduction are linked. In the formation of MgO, the four electrons gained by each oxygen molecule require that four electrons be lost by magnesium, causing two Mg atoms to form two Mg^{2+} ions. The number of electrons gained during reduction half-reaction must be equal to the number of electrons lost during oxidation half-reaction. It is impossible to have oxidation without reduction, as shown in Fig. 2.2.

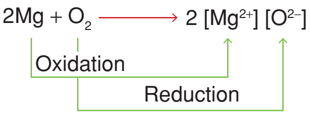


Figure 2.2 Oxidation cannot occur in the absence of reduction.

Oxidizing and Reducing Agents

1. **Oxidizing agent** is a substance that accepts electrons, and causes the other substance to lose electrons and get oxidized. (It undergoes decrease in valence.)
2. **Reducing agent** is a substance that donates electrons, and causes the other substance to gain electrons and get reduced. (It undergoes an increase in valence.)

In a redox reaction, the oxidizing agent gets reduced and the reducing agent gets oxidized. For example in the formation of sodium chloride, sodium serves as the reducing agent when it supplies electrons to chlorine and itself gets oxidized. Chlorine acts as the oxidizing agent when it accepts electrons from the sodium, gets reduced to chloride ion. Hence, for a redox reaction to occur, one substance must accept electrons from the other.

Similarly, when a piece of zinc metal is immersed in an aqueous solution of Ag^+ ions, the zinc metal donates electrons to the Ag^+ ions, and therefore reduces the Ag^+ ions. Zinc, therefore, acts as a **reducing agent** in the reaction.

The same electrons that are lost by the zinc are gained by the silver. On the other hand, the Ag^+ ions gain electrons from the zinc metal and thereby oxidize zinc. Ag^+ ion is, therefore, an **oxidizing agent**.

$$\underset{\text{Reducing agent}}{Zn(s)} + \underset{\text{Oxidizing agent}}{2Ag^+(aq)} \rightleftharpoons Zn^{2+}(aq) + 2Ag(s)$$

Solved Example 2-16

The bright light produced by the reaction between magnesium and oxygen is often used in fireworks displays. The product of the reaction is magnesium oxide, an ionic compound. Which element is oxidized and which is reduced? What are the oxidizing and reducing agents?

Solution

When a magnesium atom becomes a magnesium ion, it must lose two electrons. Since the electrons are lost in this process, they appear on the right when we express it as an equation.

$$Mg \rightarrow Mg^{2+} + 2e^-$$

By losing electrons, *magnesium is oxidized*. This also means that *Mg must be the reducing agent*. When oxygen reacts to yield O^{2-} ions, each oxygen atom must gain two electrons, so an O_2 molecule must gain four electrons. Since electrons are being gained, they appear on the left in the equation.

$$O_2 + 4e^- \rightarrow 2O^{2-}$$

By gaining electrons, O_2 *is reduced and must be the oxidizing agent*.

The complete reaction is

$$2Mg(s) + O_2(g) \rightarrow 2MgO(s)$$

Solved Example 2-17

When sodium reacts with molecular oxygen, the product is sodium peroxide, which contains the peroxide ion. Is O_2 oxidized or reduced in this reaction?

Solution

The reaction involved is $2Na(s) + O_2(g) \rightarrow Na_2O_2(s)$

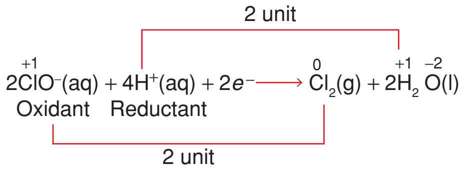
O_2 is added to electropositive element (Na), so it undergoes reduction.

Solved Example 2-18

Mixing household chemicals can be extremely dangerous to one's health. For example, mixing bleach with toilet cleaner is especially dangerous since this reaction produces water and the highly toxic chlorine gas. Write the half reaction for the conversion from the hypochlorite ion to chlorine gas. Is this half reaction representing the oxidation or reduction of Cl?

Solution

Bleach contains ClO^- ions and toilet cleaner contains acid HCl. The half-reaction is as follows:



$$\underset{\text{Oxidant}}{2\overset{+1}{Cl}O^-(aq)} + \underset{\text{Reductant}}{4H^+(aq)} + 2e^- \longrightarrow \overset{0}{Cl_2}(g) + 2\overset{+1}{H_2}\overset{-2}{O}(l)$$

This half reaction represents reduction of Cl.

Displacement Reactions and Activity Series

In displacement reactions, one metal displaces another metal from its compounds, and this is illustrated by the reaction of zinc with copper ion. Suppose a brightly polished strip of metallic zinc is dipped into a solution of copper sulphate. After the zinc strip lies in the solution for a while, a reddish brown deposit of metallic copper forms on the zinc strip. On analyzing the solution, it is found that the solution now contains zinc ions as well as some remaining unreacted copper ions.

The net ionic equation involved is as follows:

$$Zn(s) + Cu^{2+}(aq) \rightarrow Cu(s) + Zn^{2+}(aq)$$

Sulphate ion is a spectator ion in this reaction.

Note: Spectator ions are ions that stay unaffected during a chemical reaction. They appear both as reactant and as product in an ionic equation. For example, in the following ionic equation, the sodium and nitrate ions are spectator ions.

$$Ag^{+}(aq) + NO_3^{-}(aq) + Na^{+}(aq) + Cl^{-}(aq) \rightarrow AgCl(s) + Na^{+}(aq) + NO_3^{-}(aq)$$

Metallic zinc is oxidized as copper ion is reduced. In the process, Zn^{2+} ions have taken the place of the Cu^{2+} ions, so a solution of copper sulphate is changed to a solution of zinc sulphate (Fig. 2.3).

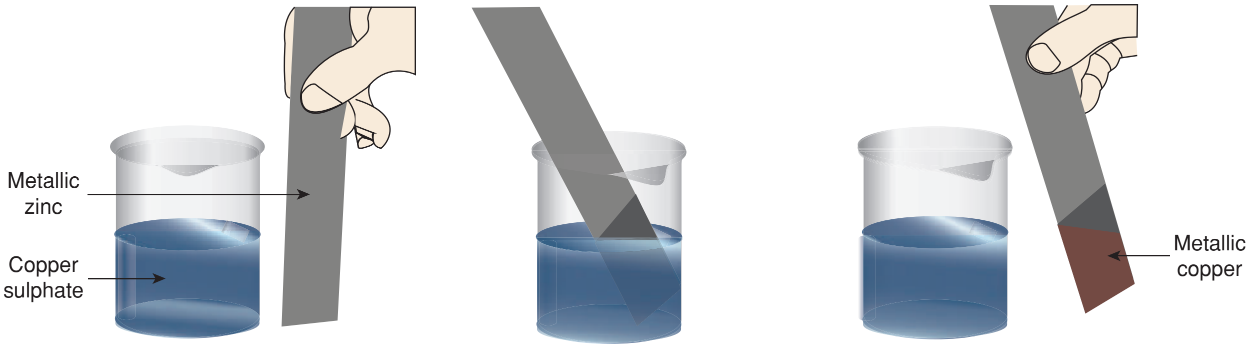


Figure 2.3 Reaction of zinc with copper ions.

Note: When hydrogen sulphide gas is passed this solution of zinc and the solution is made alkaline by adding ammonia, a white precipitate of zinc sulphide is observed.

An atomic-level view of what is happening at the surface of the zinc during the reaction is depicted in Fig. 2.4. From Fig. 2.4(a), it can be seen that copper ions (blue) collide with the zinc surface where they pick up electrons from zinc atoms (gray). The zinc atoms become zinc ions (yellow) and enter the solution. The copper ions become copper atoms (red–brown) and stick to the surface of the zinc. From Fig. 2.4(b), it can be seen that a close-up view of the exchange of electrons that leads to the reaction.

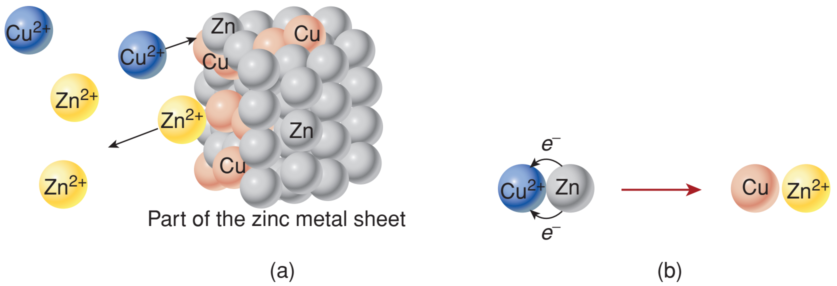


Figure 2.4 Reaction of copper ions with zinc, viewed at the atomic level.

In the reaction of zinc with copper ion as described above, zinc is more active and it displaces copper which is less active in a compound. The word active means easily oxidized. This is actually a general phenomenon: an element that is more easily oxidized will displace the one that is less easily oxidized from its compounds. The metals are placed in order of their ease of oxidation. Thus emerges the activity series shown in Table 2.2. In this table, metals at the bottom are more easily oxidized (are more active) than those at the top.

Table 2.2 Activity series for some metals (and hydrogen)

	Element	Main oxidation product
Least Active	Gold	Au^{3+}
	Mercury	Hg^{2+}
	Silver	Ag^{+}
	Copper	Cu^{2+}
	Hydrogen	H^{+}
	Lead	Pb^{2+}
	Tin	Sn^{2+}
	Cobalt	Co^{2+}
	Cadmium	Cd^{2+}
	Iron	Fe^{2+}
	Chromium	Cr^{3+}
	Zinc	Zn^{2+}
	Manganese	Mn^{2+}
	Aluminium	Al^{3+}
	Magnesium	Mg^{2+}
	Sodium	Na^{+}
	Calcium	Ca^{2+}
	Strontium	Sr^{2+}
	Barium	Ba^{2+}
	Potassium	K^{+}
	Rubidium	Rb^{+}
Most Active	Caesium	Cs^{+}

↓ Increasing tendency for oxidation to occur

↑ Increasing tendency for reduction to occur

Important observations from activity series:

1. An element will be displaced from its compounds by any metal below it in the table.
2. Metals below hydrogen in the series can displace hydrogen from solutions containing H^+. The metals above hydrogen in the table do not react with acids in which H^+ is the strongest oxidizing agent. Metals at the very bottom of the table are very easily oxidized and hence are extremely strong reducing agents. They are so reactive that they are able to reduce the hydrogen in water molecules. For example, sodium reacts vigorously with water to form sodium hydroxide.

$$2Na(s) + 2H_2O \rightarrow H_2(g) + 2NaOH(aq)$$

3. For metals below hydrogen in the activity series, there is a parallel between the ease of oxidation of the metal and the speed with which it reacts with H^+.

Solved Example 2-19

Write a chemical equation for the reaction that will occur when

(a) aluminium metal is added to a solution of copper(II) chloride and

(b) silver metal is added to a solution of magnesium sulphate.

If no reaction occurs, write "no reaction" in place of the products.

Solution

(a) $Al(s) + 3CuCl(s) \rightarrow AlCl_3 + 3Cu$

(b) $2Ag + MgSO_4 \rightarrow Ag_2SO_4 + Mg$

Solved Example 2-20

Arrange the following metals in the order in which they displace each other from the solution of their salts: Al, Cu, Fe, Mg and Zn.

Solution

A metal of stronger reducing power displaces another metal of weaker reducing power from its solution of salt. The order of the increasing reducing power of the given metals is Cu < Fe < Zn < Al < Mg. Hence, we can say that Mg can displace Al from its salt solution, but Al cannot displace Mg. Thus, the order in which the given metals displace each other from the solution of their salts is given below:

$$Mg > Al > Zn > Fe > Cu$$

2.3 | CALCULATION OF *n*-FACTOR IN A REACTION

The *n*-factor of oxidizing agent or reducing agent is calculated depending upon the change in oxidation state of the species considered. Some of the cases are discussed as follows:

1. When only one atom undergoes either reduction or oxidation:

$$\underset{n=5}{\overset{+7}{MnO_4^-}} \xrightarrow{H^+} \overset{+2}{Mn^{2+}}$$

Here the *n*-factor is (+7) × 1 – (+2) × 1 = 5.

2. When only one atom undergoes change in oxidation state but appears in two products with the same oxidation state.

$$\overset{+6\times2}{Cr_2O_7^{2-}} \longrightarrow \overset{+3}{Cr^{3+}} + \overset{3+}{Cr^{3+}}$$

Here the *n*-factor is [(+6) × 2 – (+3) × 2] = 6.

3. When only one atom undergoes change in oxidation state but forms two products with different oxidation states because of either only oxidation or only reduction.

$$3\overset{+7}{MnO_4^-} \longrightarrow 2\overset{+2}{Mn^{2+}} + \overset{+6}{Mn^{6+}}$$

For 3 mol of MnO_4^-, the total moles of electron is [2 × (+2) – 2 × (+7)] + [1 × (+6) – 1(+7)] = 4 – 14 + 6 – 7 = 11. So, for each mole of MnO_4^-, *n*-factor = 11/3.

4. When only one atom undergoes change in oxidation state in two products with changed oxidation state in one product and same oxidation state as reactant in the other product.

$$K_2Cr_2O_7 + 14HCl \rightarrow 2KCl + 2CrCl_3 + 3Cl_2 + 7H_2O$$

In this case, 14 mol of HCl are reacting, out of which 6 Cl have oxidation state 0 and 8 Cl have oxidation state –1 in $CrCl_3$ and KCl. So, the total moles of electrons lost by 14 HCl is 6. Thus, each mole of HCl takes 6/14 = 3/7 moles of electrons. So, *n*-factor = 3/7.

5. When two or more atoms in the salt undergo change in oxidation state because of either oxidation or reduction. For example,

$$FeC_2O_4 \rightarrow Fe^{3+} + 2CO_2$$

Hence, the *n*-factor of FeC_2O_4 is [1 × (+2) –1 × (+3)] + [2 × (+3) – 2 × (+4)] = 3.

6. When two atoms undergo change in oxidation state with one undergoing oxidation and other reduction. For this case, the change in oxidation state of either the atom being oxidized or the atom being reduced should be calculated. For example.

$$\overset{-3\times2}{(NH_4)_2}\overset{+6\times2}{Cr_2}O_7 \longrightarrow \overset{0\times2}{N_2} + \overset{+3\times2}{Cr_2}O_3 + 4H_2O$$

Hence, the *n*-factor of $(NH_4)_2Cr_2O_7$ considering reduction = (+6) × 2 – (+3) × 2 = 6

7. When the species undergoes disproportionation reaction, that is, the oxidant and reductant are the same species or the same element from the species is getting oxidized as well as reduced.

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

For oxidation reaction, n-factor $= 2\times 0-(-1)\times 2 = 2$ and for reduction reaction, n-factor $= (-2)\times 2-(-1)\times 2 = 2$. Hence, the n-factor of H_2O_2 either considering oxidation or reduction reaction is same, that is, 2.

Solved Example 2-21

Calculate the n-factor of HCl in the following reactions: **(a)** $KMnO_4$ with HCl and **(b)** $K_2Cr_2O_7$ with HCl.

Solution

(a) $KMnO_4$ with HCl. The reaction is

$$2\overset{+1}{K}\overset{+7}{Mn}O_4 + 16H\overset{-1}{Cl} \rightarrow 2\overset{+2}{Mn}\overset{-1}{Cl}_2 + 5\overset{0}{Cl}_2 + 2\overset{+1}{K}\overset{-1}{Cl} + 8H_2O$$

In this case, we cannot proceed by the usual method of writing half reaction, instead we need to first balance the redox reaction and then following the steps as shown.

From the reaction, we find that 2 mol of $KMnO_4 \equiv$ 16 mol of HCl, thus, we write as

$$x \text{ mol of } KMnO_4 \equiv 8x \text{ mol of HCl} \qquad (1)$$

Now, 1 gram equiv. of $KMnO_4$ reacts with 1 gram equiv. of HCl, so from the reaction

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

we have $\dfrac{1}{5}$ mol of $KMnO_4 \equiv \dfrac{1}{y}$ mol of HCl

From Eq. (1), we have

$$\frac{1}{5} \text{ mol of } KMnO_4 \equiv 8\times\frac{1}{5} \text{ mol of HCl} \equiv \frac{1}{y} \text{ mol of HCl}$$

or $y = 5/8 = n$-factor of HCl.

(b) The reaction is

$$\overset{+1}{K}_2\overset{+6}{Cr}_2O_4 + 14H\overset{-1}{Cl} \rightarrow 2\overset{+1}{K}\overset{-1}{Cl} + 2Cr\overset{-1}{Cl}_3 + 3\overset{0}{Cl}_2 + 7H_2O$$

Now, from the reaction

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

the n-factor of $K_2Cr_2O_7 = 6$.

Now, 1 mol of $K_2Cr_2O_7 \equiv$ 14 mol of HCl (1)

and gram equiv. of $K_2Cr_2O_7 \equiv$ gram equiv. of HCl, so we have

$$\frac{1}{6} \text{ mol } K_2Cr_2O_7 \equiv \frac{1}{y} \text{ mol HCl} \qquad (2)$$

From Eqs. (1) and (2), we have

$$\frac{14}{6} = \frac{1}{y} \Rightarrow y = \frac{3}{7}$$

or n-factor of HCl = 3/7.

Solved Example 2-22

In redox reaction, $Ba(MnO_4)_2$ oxidizes $K_4[Fe(CN)_6]$ into K^+, Fe^{3+}, CO_3^{2-} and NO_3^- ions in acidic medium, where $Ba(MnO_4)_2$ itself reduces into Mn^{+2}, than how many moles of $Ba(MnO_4)_2$ will react with 1 mole of $K_4[Fe(CN)_6]$

Solution

The n-factor of $Be(MnO_4)_2 = 10$ and n-factor of $K_4[Fe(CN)_6]$ = 61. Now, since

$$\frac{\text{Moles of } Ba(MnO_4)_2}{1 \text{ mol of } K_4Fe(CN)_6} = \frac{61}{10}$$

so,

$$\text{Moles of } Ba(MnO_4)_2 = \frac{61}{10}\times 1 = 6.1$$

2.4 | BALANCING OF REDOX REACTIONS

The redox reactions can be balanced by oxidation number method or by half-reaction method.

Half-Reaction (Ion Electron) Method

When $Cr_2O_7^{2-}$ reacts with Fe^{2+} in an acidic solution, Cr^{3+} and Fe^{3+} are formed as products. This information permits us to write the skeleton equation, which shows only the ions (or sometimes molecules, too) involved in the redox changes.

$$Cr_2O_7^{2-}(aq) + Fe^{2+}(aq) \rightarrow Cr^{3+} + Fe^{3+}$$

We then proceed through the steps described below to find the balanced equation. As you will see, the half-reaction or ion–electron method will tell us how H^+ and H_2O are involved in the reaction; we do not need to know this in advance.

1. **Divide the skeleton equation into half-reactions:** One of the reactants $Cr_2O_7^{2-}$ is written at the left of an arrow. On the right, we write what $Cr_2O_7^{2-}$ changes into, which is Cr^{3+}. This gives us the beginnings of one half-reaction. For the second half-reaction, the other reactant, Fe^{2+}, is written on the left and the other product, Fe^{3+}, on the right. Complete formulas should be used for the ions that appear in the skeleton equation. Except for hydrogen and oxygen, the same elements must appear on both sides of a given half-reaction.

$$Cr_2O_7^{2-}(aq) \rightarrow Cr^{3+}(aq)$$

$$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq)$$

2. **Balance atoms other than H and O:** There are two Cr atoms on the left and only one on the right, so we place a coefficient of 2 in front of Cr^{3+}. The second half-reaction is already balanced in terms of atoms, so we leave it "as is".

$$Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq)$$

$$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq)$$

3. **Balance oxygen by adding H_2O to the side that needs O:** There are seven oxygen atoms on the left of the first half-reaction and none on the right. Therefore, we add $7H_2O$ to the right side of the first half-reaction to balance the oxygen atoms. (There is no oxygen imbalance in the second half-reaction, so there is nothing to do there.)

$$Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(aq)$$

$$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq)$$

The oxygen atoms now balance, but hydrogen will be balanced next.

Note: Use H_2O, not O or O_2, to balance oxygen atoms because H_2O is what is actually present in the solution.

4. **Balance hydrogen by adding H^+ to the side that needs H:** After adding water, we see that the first half-reaction has 14 hydrogen ions on the right and none on the left. To balance hydrogen, we add $14H^+$ to the left side of the half-reaction. When you do this step (or others) *be careful to write the charges on the ions*. If they are omitted, you will not obtain a balanced equation in the end.

$$14H^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

$$Fe^{2+} \rightarrow Fe^{3+}$$

Now each half-reaction is balanced in terms of atoms. The charge will be balanced next.

5. **Balance the charge by adding electrons:** First we compute the net electrical charge on each side. For the first half-reaction we have

$$\underbrace{14H^+ + Cr_2O_7^{2-}}_{\text{Net charge} \;=\; (14+) \;+\; (2-) \;=\; 12+} \quad \rightarrow \quad \underbrace{2Cr^{3+} + 7H_2O}_{\text{Net charge} \;=\; 2(3+) \;+\; 0 \;=\; 6+}$$

The algebraic difference between the net charges on the two sides equals the number of electrons that must be added to the more positive (or less negative) side: Here, $6e^-$ is added to the left side of the half-reaction.

$$6e^- + 14H^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

This half-reaction is now complete; it is balanced in terms of both atoms and charge. To balance the other half-reaction, we add one electron to the right.

$$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$$

6. **Make the number of electrons gained equal to the number lost and then add the two half-reactions:** At this point we have the two balanced half-reactions.

$$6e^- + 14H^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$
$$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$$

Six electrons are gained in the first, but only one is lost in the second. Therefore, before combining the two equations we multiply all of the coefficients of the second half-reaction by 6. We do this because in a redox reaction, the number of electrons gained by the atoms which get reduced is equal to the number of electrons lost by the atoms which get oxidized.

$$\begin{array}{r} 6e^- + 14H^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) \\ [Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-] \times 6 \\ \hline \text{Sum: } 6e^- + 14H^+(aq) + Cr_2O_7^{2-}(aq) + 6Fe^{2+}(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) + 6Fe^{3+}(aq) + 6e^- \end{array}$$

7. **Cancel anything that is the same on both sides:** This is the final step. Six electrons cancel from both sides to give the final balanced equation.

$$14H^+(aq) + Cr_2O_7^{2-}(aq) + 6Fe^{2+}(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) + 6Fe^{3+}(aq)$$

In some reactions, after adding the two half-reactions H_2O or H^+ are also there on both sides; for example, $6H_2O$ on the left and $2H_2O$ on the right. These have to be cancelled. Thus,

$$\ldots + 6H_2O \ldots \rightarrow \ldots + 2H_2O \ldots \text{ reduces to } \ldots + 4H_2O \ldots \rightarrow \ldots$$

In a basic solution, the concentration of H^+ is very small; the dominant species are H_2O and OH^-. Strictly speaking, these should be used to balance the half-reactions. However, the simplest way to obtain a balanced equation for a basic solution is to first *assume* that the solution is acidic. We balance the equation using the seven steps just described, and then we use a simple three-step procedure described below to convert the equation into the correct form for a basic solution. The conversion uses the fact that H^+ and OH^- react in a 1:1 ratio to give H_2O. The additional steps in the half-reaction method for basic solutions are as follows:

8. Add to *both* sides of the equation the same number of OH^- as there are H^+.
9. Combine H^+ and OH^- to form H_2O.
10. Cancel any H_2O that you can.

As an example, suppose we wanted to balance the following equation for a basic solution:

$$SO_3^{2-}(aq) + MnO_4^-(aq) \rightarrow SO_4^{2-}(aq) + MnO_2(s)$$

On following Steps 1–7 for acidic solutions, we get

$$2H^+(aq) + 3SO_3^{2-}(aq) + 2MnO_4^-(aq) \rightarrow 3SO_4^{2-}(aq) + 2MnO_2(s) + H_2O(l)$$

Conversion of this equation to one appropriate for a basic solution proceeds as follows.

Add to both sides of the equation the same number of OH^- as there are H^+. The equation for acidic solution has $2H^+$ on the left, so we add $2OH^-$ to *each* side. This gives

$$2OH^-(aq) + 2H^+(aq) + 3SO_3^{2-}(aq) + 2MnO_4^-(aq) \rightarrow 3SO_4^{2-}(aq) + 2MnO_2(s) + H_2O(l) + 2OH^-(aq)$$

Combine H^+ and OH^- to form H_2O. The left side has $2OH^-$ and $2H^+$, which become $2H_2O$. So in place of $2OH^- + 2H^+$ we write $2H_2O$.

$$\underbrace{2OH^-(aq) + 2H^+(aq)}_{\downarrow} + 3SO_3^{2-}(aq) + 2MnO_4^-(aq) \rightarrow 3SO_4^{2-}(aq) + 2MnO_2(s) + H_2O(l) + 2OH^-(aq)$$

$$2H_2O(l) + 3SO_3^{2-}(aq) + 2MnO_4^-(aq) \rightarrow 3SO_4^{2-}(aq) + 2MnO_2(s) + H_2O(l) + 2OH^-(aq)$$

Cancel H_2O. In this equation, one H_2O can be eliminated from both sides. The final equation, balanced for basic solution, is

$$H_2O(l) + 3SO_3^{2-}(aq) + 2MnO_4^-(aq) \rightarrow 3SO_4^{2-}(aq) + 2MnO_2(s) + 2OH^-(aq)$$

Solved Example 2-23

In passing chlorine gas through a concentrated solution of alkali, we get chloride and chlorate ions. Obtain the balanced chemical equation for this reaction.

Solution

The skeletal equation for the given reaction is

$$\mathrm{Cl_2(g) + OH^-(aq) \longrightarrow Cl^-(aq) + ClO_3^-(aq)}$$

Here, the oxidation number of Cl_2 increases from 0 to +5 in ClO_3^- and decreases to −1 in Cl^-. Hence, Cl_2 acts as an oxidant as well as reductant.

Hence, the total increase in oxidation of $Cl_2 = 2 \times 5 = 10$

Total decrease in oxidation number of $Cl_2 = 2 \times (-1) = -2$

Reduction half-reaction

$$\mathrm{Cl_2(g) \rightarrow Cl^-(aq)}$$

The Cl atoms are balanced by multiplying the reaction by 2,

$$\mathrm{Cl_2(g) \rightarrow 2Cl^-(aq)}$$

To balance oxidation number, we add 2 electrons to RHS of the equation to get

$$\mathrm{Cl_2(g) + 2}e^- \mathrm{\rightarrow 2Cl^-(aq)} \qquad (1)$$

Thus, Eq. (1) represents the balanced reduction half-reaction.

Oxidation half-reaction

$$\mathrm{Cl_2(g) \rightarrow ClO_3^-(aq)}$$

To balance all atoms other than O and H, multiply ClO_3^- by 2, we have,

$$\mathrm{Cl_2(g) \rightarrow 2ClO_3^-(aq)}$$

The oxidation number is balanced by adding 10 electrons to RHS of the equation

$$\mathrm{Cl_2(g) \rightarrow 2ClO_3^-(aq) + 10}e^-$$

Balance the charge by adding 12OH⁻ ions to the LHS, since the reaction occurs in the basic medium.

$$\mathrm{Cl_2(g) + 12OH^-(aq) \rightarrow 2ClO_3^-(aq) + 10}e^-$$

To balance O atoms, we add $6H_2O$ to the RHS to get

$$\mathrm{Cl_2(g) + 12OH^-(aq) \rightarrow 2ClO_3^-(aq) + 6H_2O(l) + 10}e^- \qquad (2)$$

Therefore, Eq. (2) represents the balanced oxidation half-reaction. To balance the electrons gained in Eq. (1) and lost in Eq. (2), we multiply Eq. (1) by 5 and add this to Eq. (2), to get

$$\begin{array}{l} \mathrm{5Cl_2(g) + 10}e^- \mathrm{\rightarrow 10Cl^-(aq)} \\ \mathrm{Cl_2(g) + 12OH^-(aq) \rightarrow 2ClO_3^-(aq) + 6H_2O(l) + 10}e^- \\ \hline \mathrm{6Cl_2(g) + 12OH^-(aq) \rightarrow 10Cl^-(aq) + 2ClO_3^-(aq) + 6H_2O(l)} \end{array}$$

or $\mathrm{3Cl_2(g) + 6OH^-(aq) \rightarrow 5Cl^-(aq) + ClO_3^-(aq) + 3H_2O(l)}$

This represents the final balanced redox reaction.

Solved Example 2-24

The element technetium (atomic number 43) is radioactive and one of its isotopes, ^{99}Tc, is used in medicine for diagnostic imaging. The isotope is usually obtained in the form of the pertechnetate anion, TcO_4^-, but its use sometimes requires the technetium to be in a lower oxidation state. Reduction can be carried out using Sn^{2+} in an acidic solution. The skeleton equation is

$$\mathrm{TcO_4^- + Sn^{2+} \rightarrow Tc^{4+} + Sn^{4+}} \ \text{(acidic solution)}$$

Balance the equation by the ion–electron method.

Solution

First, we break the given reaction into half-reactions:

$$\mathrm{TcO_4^- \rightarrow Tc^{4+}} \text{ and } \mathrm{Sn^{2+} \rightarrow Sn^{4+}}$$

Each half-reaction is already balanced with respect to atoms other than O and H, so next we balance the O atoms by using water:

$$\mathrm{TcO_4^- \rightarrow Tc^{4+} + 4H_2O \rightarrow}$$

$$\mathrm{Sn^{2+} \rightarrow Sn^{4+} +}$$

Now we balance H by using H^+:

$$\mathrm{8H^+ + TcO_4^- \rightarrow Tc^{4+} + 4H_2O}$$

$$\mathrm{Sn^{2+} \rightarrow Sn^{4+}}$$

Next, we add electrons to balance the charges on both sides of the equations:

$$3e^- \mathrm{+ 8H^+ + TcO_4^- \rightarrow Tc^{4+} + 4H_2O}$$

$$Sn^{2+} \rightarrow Sn^{4+} + 2e^-$$

We multiply the equations so that the electrons gained equals the electrons lost and adding them we have our balanced equation

$$(3e^- + 8H^+ + TcO_4^- \rightarrow Tc^{4+} + 4H_2O) \times 2$$
$$(Sn^{2+} \rightarrow Sn^{4+} + 2e^-) \times 3$$
$$\overline{3Sn^{2+} + 16H^+ + 2TcO_4^- \rightarrow 2Tc^{4+} + 8H_2O + 3Sn^{4+}}$$

Solved Example 2-25

Explain why the following equation is not balanced. Balance it using the half-reaction method.

$$Al(s) + Cu^{2+}(aq) \rightarrow Al^{3+}(aq) + Cu(s)$$

Solution

The equation is not balanced because the number of charges on both sides of the equation is not balanced. To balance the equation by half-reaction method, we first divide the skeletal equation into two half-reaction:

$$Al \rightarrow Al^{3+}$$
$$Cu^{2+} \rightarrow Cu$$

In the second step, we add the required number of electrons to the half-reactions and balance the number of charges:

$$Al \rightarrow Al^{3+} + 3e^-$$
$$Cu^{2+} + 2e^- \rightarrow Cu$$

In the third step, we balance the atoms in the half-reactions

$$Al \rightarrow Al^{3+} + 3e^- \qquad \text{(Oxidation)}$$
$$Cu^{2+} + 2e^- \rightarrow Cu \qquad \text{(Reduction)}$$

Next we add the balanced half-reactions. To balance the gain and loss of electrons, we multiply oxidation half-reaction with 2 and reduction half-reaction with 3, so that number of electrons on both sides cancels out.

$$(Al \rightarrow Al^{3+} + 3e^-) \times 2$$
$$(Cu^{2+} + 2e^- \rightarrow Cu) \times 3$$
$$\overline{2Al + 3Cu^{2+} \rightarrow 2Al^{3+} + 3Cu}$$

So the balanced equation is:

$$2Al(s) + 3Cu^{2+}(aq) \rightarrow 2Al^{3+}(aq) + 3Cu(s)$$

Oxidation Number Method

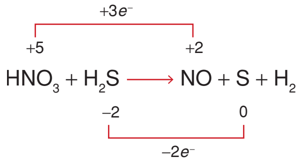
In a typical redox reaction, only two atoms undergo a change in their oxidation states. By identifying these two atoms and calculating the change in the oxidation state, we can arrive at a balanced equation. The **oxidation number** method focuses on the atoms of the elements undergoing a change in oxidation state. The following reaction will be used to illustrate the procedures for balancing equations by the oxidation state method.

$$HNO_3(aq) + H_2S(aq) \rightarrow NO(g) + S(s) + H_2O(l)$$

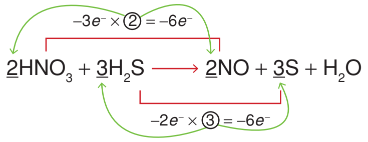
1. Represent each reactant and product with correct formula.
2. Identify the atoms whose oxidation states have changed.

$$H\overset{+5}{N}O_3 + H_2\overset{-2}{S} \rightarrow \overset{+2}{N}O + \overset{0}{S} + \overset{+1}{H_2}\overset{-2}{O}$$

3. Make sure that the number of atoms of nitrogen are equal on both sides of the equation and similarly make sure that the number of atoms of sulphur are equal on both sides of the equation (i.e., the equation is balanced). Then find the increase (or decrease) in the oxidation number for the number of atoms involved.
4. Draw a bridge between the same atoms whose oxidation states have changed, indicating the electrons gained or lost. This corresponds to the change in oxidation number of atom.



5. Multiply the molecule, atoms or ions oxidized or reduced by an appropriate number so as to make the increase in the oxidation number of the atom(s) oxidized equal to the decrease in the oxidation number of the atom(s) reduced. In this example, multiply the two numbers (+3 and –2) by whole numbers that produce a common multiple. For 3 and 2, the common multiple is 6. (e.g., $+3 \times 2 = +6$; $-2 \times \underline{3} = -6$.) Use these multipliers as coefficients of the respective compounds or elements. Note that six electrons are lost (bottom) and six are gained (top).


$-3e^- \times ② = -6e^-$
$\underline{2}HNO_3 + \underline{3}H_2S \longrightarrow \underline{2}NO + \underline{3}S + H_2O$
$-2e^- \times ③ = -6e^-$

6. Balance the rest of the equation by inspection. Note that there are eight H's on the left, so *four* H_2O's are needed on the right. If the equation has been balanced correctly, the O's should balance. Note that they do. The final balanced equation is

$$2HNO_3 + 3H_2S \rightarrow 2NO + 3S + 4H_2O$$

Fastest Method for Balancing an Equation

Consider the following reaction

$$MnO_4^- + Cl^- \rightarrow Cl_2 + Mn^{2+}$$

The fastest method for balancing this equation involves the following steps.

Step 1: Choose any side (LHS or RHS) and write the *n* factors of the same on top of the compounds. Say, we choose LHS in the above equation.

Step 2: Cross multiply the *n*-factors. Now, we do not change the coefficients of this side.

$$1\ MnO_4^- + 5\ Cl^- \rightarrow Cl_2 + Mn^{2+}$$

Step 3: Balance the elements getting oxidized or reduced on the other side. In this case, we have to balance Mn and Cl on the other side.

$$1\ MnO_4^- + 5\ Cl^- \rightarrow Cl_2 + Mn^{2+}$$

Step 4: Balance O atoms by addition of H_2O

$$1\ MnO_4^- + 5\ Cl^- \rightarrow \frac{5}{2}Cl_2 + 1Mn^{2+} + 4H_2O$$

Step 5: Balance H atoms by addition of H^+

$$8\,H^+ + 1\ MnO_4^- + 5\ Cl^- \rightarrow \frac{5}{2}Cl_2 + 1Mn^{2+} + 4H_2O$$

The above is new balanced equation in acidic medium. In order to balance the equation in basic medium, repeat Steps 1–5 and then add $OH^- = H^+$ on both sides and cancel H_2O.

$$8\,OH^- + 8\,H^+ + 1\ MnO_4^- + 5\ Cl^- \rightarrow \frac{5}{2}Cl_2 + 1Mn^{2+} + 4H_2O + 8\,OH^-$$

$$8\,H_2O + 1\ MnO_4^- + 5\ Cl^- \rightarrow \frac{5}{2}Cl_2 + 1Mn^{2+} + 4H_2O + 8\,OH^-$$

Subtracting H_2O, we get the final equation in basic medium.

$$4H_2O + 1\ MnO_4^- + 5\ Cl^- \rightarrow \frac{5}{2}Cl_2 + 1Mn^{2+} + 8\,OH^-$$

Note: No additional step is required to balance the charge in any equation.

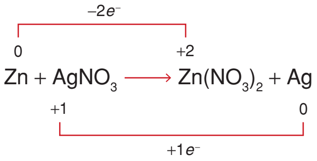
Solved Example 2-26

Balance the following equation by the oxidation number method.

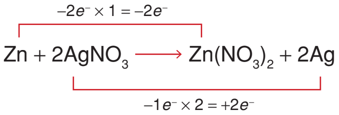
$$Zn + AgNO_3 \to Zn(NO_3)_2 + Ag$$

Solution

The equation can be represented as



The oxidation (top) should be multiplied by 1, and the reduction process (bottom) should be multiplied by 2.



The final balanced equation is

$$Zn + 2AgNO_3 \to Zn(NO_3)_2 + 2Ag$$

Solved Example 2-27

When very dilute nitric acid reacts with a strong oxidizing agent such as magnesium, the nitrate ion is reduced to ammonium ion. Write a balanced net ionic equation for the reaction.

Solution

The reaction involved is $HNO_3 + Mg \to NH_4^+ + Mg^{2+}$
Divide the reaction into two half-reactions and balance the number of atoms

$$HNO_3 \to NH_4^+$$

$$Mg \to Mg^{2+}$$

$$HNO_3 \to NH_4^+ + 3H_2O$$

$$Mg \to Mg^{2+}$$

$$HNO_3 + 9H^+ \to NH_4^+ + 3H_2O$$

$$Mg \to Mg^{2+}$$

Balance the charges with electrons

$$8e^- + HNO_3 + 9H^+ \to NH_4^+ + 3H_2O$$

$$Mg \to Mg^{2+} + 2e^-$$

Multiply by a factor to make the number of electrons the same

$$8e^- + HNO_3 + 9H^+ \to NH_4^+ + 3H_2O$$

$$(Mg \to Mg^{2+} + 2e^-) \times 4$$

Add together, we get $HNO_3 + 9H^+ + 4Mg \to NH_4^+ + 4Mg^{2+} + 3H_2O$

Solved Example 2-28

In the balanced chemical reaction:

$$1O_3^- + aI^- + bH^+ \to cH_2O + dI_2$$

what are *a*, *b*, *c* and *d*, respectively,

Solution

Let us proceed stepwise to determine the products. First, I^- undergoes oxidation to form I_2

$$I^- \to I_2$$

Now, iodate ion undergoes reduction as follows: $IO_3^- \to I_2$
Adding H^+ and H_2O to balance the number of O atoms, we get

$$IO_3^- + 12H^+ \to I_2 + 6H_2O$$

Balancing the charges with electrons, we get

$$IO_3^- + 12H^+ + 10e^- \to I_2 + 6H_2O \qquad (1)$$

$$2I^- \to I_2 + 2e^- \qquad (2)$$

Multiplying Eq. (1) by 5 to make the number of electrons same and adding with Eq. (2), we get

$$2IO_3^- + 10e^- + 12H^+ \to I_2 + 6H_2O$$

$$(I^- \to I^- + 2e^-) \times 5$$

$$\underline{\overline{2IO_3^- + 10I^- + 12H^+ \to 6I_2 + 6H_2O}}$$

Dividing throughout by 2, we get

$$IO_3^- + 5I^- + 6H^+ \to 3I_2 + 3H_2O$$

Comparing with the given equation, we get *a* = 5, *b* = 6, *c* = 3 and *d* = 3.

Solved Example 2-29

Balance each of the following equations by the oxidation number method.

(a) $NH_3 + O_2 \rightarrow NO + H_2O$

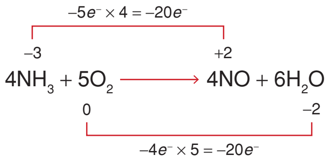
(b) $Sn + HNO_3 \rightarrow SnO_2 + NO_2 + H_2O$

(c) $Cr_2O_3 + Na_2CO_3 + KNO_3 \rightarrow CO_2 + Na_2CrO_4 + KNO_2$

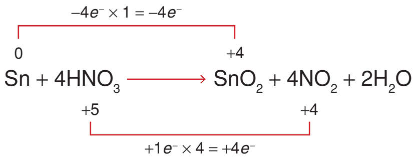
(d) $Se + BrO_3^- + H_2O \rightarrow H_2SeO_3 + Br^-$

Solution

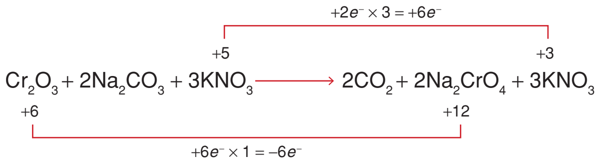
(a) The reaction can be represented as



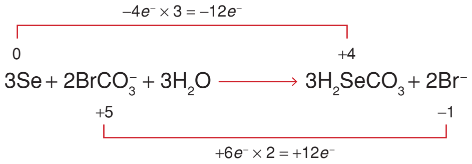
(b) The reaction can be represented as



(c) Before the number of electrons lost is calculated, notice that a temporary coefficient of "2" is needed for the Na_2CrO_4 in the products since there are 2 Cr's in Cr_2O_3 in the reactants.



(d) The reaction can be represented as



Solved Example 2-30

In the equation: $Zn + NO_3^- + OH^- \rightarrow Zn\,O_2^{2-} + NH_3$, what are the stoichiometry coefficients of Zn, NO_3^-, OH^+?

Solution

First, we find the oxidation states of atoms undergoing redox changes.

$$\overset{0}{Zn} + \overset{+5}{N}O_3^- + OH^- \rightarrow \overset{+2}{Zn}O_2^{2-} + \overset{-3}{N}H_3$$

Then we find the changes in oxidation states and equalize the species, undergoing redox change, with a suitable integer.

$$\overset{0}{Zn} + \overset{+5}{N}O_3^- + OH^- \rightarrow \overset{+2}{Zn}O_2^{2-} + \overset{-3}{N}H_3$$

Increase in oxidation state = 2 × 4 and decrease in oxidation state = 8.

Then, we multiply Zn by 4 to equalize the change in oxidation states.

$$4Zn + NO_3^- + OH^- \rightarrow 4ZnO_2^{2-} + NH_3$$

Next, we find the total charges on both the sides and find the difference in charges.

Charge on LHS = (–1) + (–1) = –2 and Charge on RHS = 4 × (–2) = –8

Difference of charges = –8 – (–2) = –6

Now, since reaction is taking place in alkaline medium, we will have to add 6 OH^- on the side falling short in negative charges, that is, LHS to equalize the charges on both the sides.

$$4Zn + NO_3^- + 7OH^- \rightarrow 4ZnO_2^{2-} + NH_3$$

Finally, we add the required number of water molecules (i.e., $2H_2O$) on the side deficient in H and O atoms to get the balance equation as

$$4Zn + NO_3^- + 7OH^- \rightarrow 4ZnO_2^{2-} + NH_3 + 2H_2O$$

2.5 | CONCEPT OF EQUIVALENT MASS

Equivalent mass is the number of parts by mass of a substance which combines or displaces (directly or indirectly) 1.008 parts by mass of hydrogen or 8 parts by mass of oxygen or 35.5 parts by mass of chlorine or 108 parts by mass of silver. Equivalent mass is related to the atomic mass by the relation:

$$\text{Equivalent mass} = \frac{\text{Atomic mass of element}}{\text{Valence } (n)}$$

when it combines with n parts by mass of hydrogen.

The equivalent weights of acids, bases and oxidizing/reducing agents can be obtained as follows:

1. **Equivalent weight of an acid:** The ratio of molecular weight of acid to basicity of acid or the ratio of molecular weight of acid to the number of replaceable hydrogen atoms in one molecule of acid.
2. **Equivalent weight of a base:** The ratio of molecular weight of base to acidity of acid or the ratio of molecular weight of base to the number of replaceable OH^- groups in one molecule of base.
3. **Equivalent weight of an oxidizing or reducing agent:** The ratio of molecular weight of the substance to the number of electrons gained or lost by one molecule in a redox reaction.

The equivalent mass of an element can be determined by any of the following methods:

1. **Hydrogen displacement method:** A known mass of metal is reacted with mineral acid and the amount of hydrogen liberated is measured under experimental conditions, and the volume of hydrogen determined at STP. The equivalent mass of metal is calculated using the mass of hydrogen (density = 0.00009 at STP), using the relation

$$\text{Equivalent mass} = \frac{\text{Mass of element}}{\text{Mass of hydrogen}} \times 1.008 = \frac{\text{Mass of element}}{\text{Volume of hydrogen displaced} \times 0.00009} \times 1.008$$

2. **Oxide formation method:** A known mass of the element is converted into its oxide directly or indirectly and the equivalent mass of the element is determined using the relation:

$$\text{Equivalent mass} = \frac{\text{Mass of element}}{\text{Mass of oxide} - \text{Mass of element}} \times 8 = \frac{\text{Mass of element}}{\text{Mass of oxygen}} \times 8$$

3. **Chloride formation method:** A known mass of element is converted into its chloride directly or indirectly and the equivalent mass of the element is determined using the relation:

$$\text{Equivalent mass} = \frac{\text{Mass of element}}{\text{Mass of chloride} - \text{Mass of element}} \times 35.5 = \frac{\text{Mass of element}}{\text{Mass of chlorine}} \times 35.5$$

4. **Metal-to-metal displacement method:** A less active metal is displaced from its salt solution by adding a known weight of more active metal and the precipitated metal is filtered, dried and weighed accurately. The equivalent masses of the metals (E_1 and E_2) are in the ratio of their respective masses (m_1 and m_2), that is,

$$\frac{m_1}{m_2} = \frac{E_1}{E_2}$$

If the equivalent weight of one of the metals is known, we can calculate the equivalent weight of the other metal.

5. **Double decomposition method:** For a double decomposition reaction of the type

$$\text{AB} + \text{CD} \rightarrow \text{AD} + \text{CB}$$

The masses of the reactants and the products are in the ratio of their equivalent masses and the equivalent mass of a compound (say AB) is the sum of equivalent masses of the radicals (A + B). Therefore,

$$\frac{\text{Mass of AB}}{\text{Mass of AD}} = \frac{\text{Equivalent mass of AB}}{\text{Equivalent mass of AD}} = \frac{\text{Equivalent mass of A} + \text{Equivalent mass of B}}{\text{Equivalent mass of A} + \text{Equivalent mass of D}}$$

Normality

Normality is defined as the number of gram equivalents of a solute dissolved per liter of solution. Mathematically, it is expressed as

$$N = \frac{\text{Number of gram equivalents}}{\text{Volume in mL}} \times 1000$$

where number of gram equivalents can be found as follows:

$$\text{Number of gram equivalents} = \frac{\text{Given weight}}{\text{Equivalent weight}}$$

Milliequivalents of the solute can be found as

$$\text{Milliequivalent of solute} = N \times V(\text{in mL}) = \frac{\text{Weight of solute}}{\text{Equivalent weight of solute}} \times 1000$$

Relationship between normality and molarity:

We know that,

$$\text{Strength of the solution (g L}^{-1}) = \text{Molarity} \times \text{Molecular mass}$$

Also,

$$\text{Strength of the solution (g L}^{-1}) = \text{Normality} \times \text{Equivalent mass}$$

Equating both relations, we get

$$\text{Molarity} \times \text{Molecular mass} = \text{Normality} \times \text{Equivalent mass}$$

or

$$\frac{\text{Normality}}{\text{Molarity}} = \frac{\text{Molecular mass}}{\text{Equivalent mass}} = n$$

Therefore,

$$\text{Normality} = n \times \text{Molarity}$$

Solved Example 2-31

A solid element with specific heat 1 J g^{-1} K^{-1}. If the equivalent weight of the element is 9. Identify the element after determining its atomic weight.

Solution

According to Dulong and Petit's law, atomic weight × specific heat (in cal g^{-1}) = 6.4. Given that specific heat = 1 J g^{-1} K^{-1}. Therefore,

$$\text{Atomic weight} = \frac{6.4}{\text{Specific heat}} = \frac{6.4}{1/4.18 \text{ cal g}^{-1}\text{K}^{-1}}$$

$$= 6.4 \times 4.18 = 26.75$$

Now, valency = atomic weight/equivalent weight = $(6.4 \times 4.18)/9 \approx 3$.

Thus, the atomic weight = equivalent weight × valency = $9 \times 3 = 27$, which is the atomic weight of Al.

Solved Example 2-32

A metal oxide has 40% oxygen. What is its equivalent weight?

Solution

The 100 g of sample of metal oxide contains 40 g of oxygen and 60 g of metal, M.

By the definition of equivalent mass, we have

$$\frac{60}{40} \times 8 = 12 \text{ g equiv.}$$

Solved Example 2-33

In the reaction $I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$, what is the equivalent weight of iodine? (At. wt. of iodine = 123.9 u)

Solution

The half reaction is $I_2 + 2e^- \rightarrow 2I^-$. Therefore,

$$\text{Equivalent weight of iodine} = \frac{1}{2} \times \text{Mol. wt.} = \frac{1}{2} \times 2 \times 123.9$$

$$= 123.9 \text{ g equiv.}$$

Solved Example 2-34

A solution of H_2O_2 labeled as 20 volumes was left open. Due to this some decomposition of some H_2O_2, the volume strength of the solution decreased. To determine the new volume strength of the H_2O_2 solution, 10 mL of the solution was taken and it was diluted to 100 mL. 10 mL of this diluted solution was titrated against 25 mL of 0.0245 M $KMnO_4$ solution under acidic condition. Calculate the volume strength of the H_2O_2 solution.

Solution

We know that milliequiv. of H_2O_2 in 10 mL = milliequiv. of $KMnO_4 = 0.0245 \times 5 \times 25 = 3.0625$ milliequiv.

Therefore, in 100 mL = 3.0625×10 milliequiv. Since 100 mL solution contains 30.625×10^{-3} equiv.

Then in 1000 mL, the normality

$$= 30.625 \times 10^{-3} \times \frac{1000}{100}$$

$$= 30.625 \times 10^{-2} = 0.30625\ \text{N}$$

Now, normality N = volume strength/5.6. So, volume strength = $N \times 5.6 = 0.30625 \times 5.6 = 1.715$ g/L

Solved Example 2-35

A polyvalent metal weighting 0.1 g and having atomic weight of 50 reacted with dilute H_2SO_4 to give 44.8 mL of hydrogen at STP. The solution containing the metal in this lower oxidation state, was found to require 60 mL of 0.1 N $KMnO_4$ solution for complete oxidation. What are valencies of metal?

Solution

The reaction involved is $\text{Metal(M)} + H_2SO_4 \rightarrow H_2$

$$44.8\ \text{mL}\ H_2\ \text{at STP} \equiv \frac{44.8}{22400}\ \text{mol of}\ H_2$$

Now, milliequiv. of M = milliequiv. of H_2O

Thus, in the reaction $M - xe^- \rightarrow M^{x+}$, $x = 2$ or oxidation state is + 2.

Now M^{2+} will acquire higher oxidation state when oxidized by $KMnO_4$

$$M^{2+} - ne^- \rightarrow M^{2+n}$$

Now, milliequiv. of M^{2+} = milliequiv. of $KMnO_4$

$$\frac{0.1}{50/n} \times 1000 = 0.1 \times 60 \Rightarrow n = 2$$

So oxidation state of M is $M^{2+n} \equiv M^{+5}$. Hence, the possible valencies of the metal are + 2 and + 5.

Note: For hydrogen, the reaction is $2H^+ + 2e^- \rightarrow H_2$
Milliequiv. of $H_2 = 2 \times$ moles of H_2

or
$$\frac{0.1}{50/x} = \left(\frac{44.8}{2200}\right) \times 2 \Rightarrow x = 2$$

2.6 | STOICHIOMETRY OF REDOX REACTIONS AND CONCEPT OF GRAM EQUIVALENTS

The quantitative relationship between reactants and products in case of redox reactions are calculated similarly as in case of general chemical reactions. The first mandatory step is to write a balanced chemical equation for the redox reaction. The coefficient of the reductant and oxidant will tell us the exact number of moles of each taking part in the redox reaction. If the stoichiometric coefficients of the reductant and oxidant are n_1 and n_2, respectively, then in a volumetric estimation, the molarity equation may be written as

$$\frac{M_1V_1}{n_1} = \frac{M_2V_2}{n_2}$$

The equation can be used for the calculation of any one variable out of the four, if the other three are known.

From the concept of gram equivalents, we have for the reaction

$$\mathrm{A + B \rightarrow C + D}$$

where A is the reducing agent and B is the oxidizing agent,

$$1\text{ g equiv. of A} \equiv 1\text{ g equiv. of B} \equiv 1\text{ g equiv. of C} \equiv 1\text{ g equiv. of D}$$

$$\text{Milliequiv. of oxidizing agent} \equiv \text{Milliequiv. of reducing agent}$$

The equivalent weights for oxidizing and reducing agents can be found as follows:

$$\text{Equivalent weight of oxidant/reductant} = \frac{\text{Molecular weight of oxidant/reductant}}{\text{Number of electrons lost/gained by one mole of reductant/oxidant}}$$

or

$$\text{Equivalent weight} = \frac{\text{Molecular weight}}{n}$$

where n is the number of electrons lost/gained by 1 mol of oxidizing/reducing agent in their balanced half reaction. Here n is known as ***n*-factor** or **valence factor**. It is an integer that relates stoichiometric quantities.

Some examples are given as follows:

1. Equivalent weights of oxidants and reductants:

$Fe_2(SO_4)_3$ as oxidizing agent:

$$Fe^{3+} + 1e^- \rightarrow Fe^{2+}$$

1 mol of $Fe_2(SO_4)_3 \equiv 2$ mol of Fe^{2+}

So $n = 2$ for 1 mol of $Fe_2(SO_4)_3$ and

$$\text{Equiv. weight} = \frac{400}{2} = 200$$

$(COOH)_2$ as reducing agent:

$$C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-$$

$$n = 2, \text{ so equiv. weight} = \frac{90}{2} = 45$$

2. Equivalent weight based on medium

$KMnO_4$ as oxidizing agent in acidic medium:

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

$$n = 5, \text{ so Equiv. weight} = \frac{158}{5} = 31.6$$

$KMnO_4$ as oxidizing agent in alkaline medium:

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

$$n = 5, \text{ so Equiv. weight} = \frac{158}{5} = 31.6$$

$Na_2S_2O_3$ as reducing agent in acidic medium:

$$2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^-$$

$$n = 2/2 = 1 \text{ for 1 mol of } Na_2S_2O_3, \text{ so Equiv. weight} = \frac{158}{1} = 158$$

$Na_2S_2O_3$ as reducing agent in alkaline medium:

$$S_2O_3^{2-} + 10OH^- \rightarrow 2SO_4^{2-} + 5H_2O + 8e^-$$

$$n = 8 \text{ for 1 mol of } Na_2S_2O_3, \text{ so Equiv. weight} = \frac{158}{8} = 19.75$$

3. Equivalent weight based on dilution

From n-factor calculation, we know that higher the n-factor, stronger is the oxidizing power. However, this rule is violated in case of HNO_3, where conc. HNO_3 is a stronger oxidizing agent. Thus, for the three cases, the number of electrons involved in the reaction is found from the standard electrode potential values.

conc. HNO_3:

$$NO_3^- + 2H^+ + 1e^- \rightarrow NO_2 + H_2O$$

$$n = 1, \text{ so Equiv. weight} = \frac{63}{1} = 63$$

dil. HNO_3:

$$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$$

$$n = 3, \text{ so Equiv. weight} = \frac{63}{3} = 21$$

4. Equivalent weight of a substance undergoing disproportionation:

Suppose a substance AX is undergoing disproportionation, then we have

$$\text{Equivalent weight} = \frac{\text{Effective mol. wt. of AX}}{\text{Number of } e^- \text{ transferred}} = \frac{\text{Mol. wt. of AX in oxidation half-reaction} + \text{Mol. wt. of AX in reduction half-reaction}}{\text{Number of } e^- \text{ transferred}} \quad (2.1)$$

The denominator containing number of electrons transferred can be same or different in the oxidation and reduction half-cell reactions. Both the cases are discussed as follows:

(a) When number of transferred electrons is same: Consider the following reaction

$$H_2O_2 \rightarrow H_2O + O_2$$

The half cell reactions are as follows:

Oxidation: $H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$
Reduction: $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$

So, $n = 2$ and effective molecular weight $= 34 + 34 = 68$. Thus, equivalent weight $= \frac{68}{2} = 34$

(b) When number of transferred electrons is different: Consider the following reaction

$$Br_2 + OH^- \rightarrow Br^- + BrO_3^- + H_2O$$

Oxidation: $Br_2 + 12OH^- \rightarrow 2BrO_3^- + 6H_2O + 10e^-$
Reduction: $(Br_2 + 2e^- \rightarrow 2Br^-) \times 5$

So, $n = 10$ and effective molecular weight $= 79.9 + 5 \times 79.9 = 479.4$. Thus,

$$\text{Equivalent weight} = \frac{479.4}{10} = 47.94$$

2.7 | VOLUMETRIC ANALYSIS

Volumetric analysis, also known as titrimetric analysis, refers to the quantitative chemical analysis carried out for calculating the volume of a solution of unknown concentration. In this technique, the exact volume of a standard solution of accurately known concentration which is required to react with the measured volume of the solution of substance is determined. This process of adding the standard solution until the reaction is just complete is called titration.

The following types of reactions are used in volumetric analysis:

1. **Precipitation reaction:** This reaction involves the formation of a sparingly soluble salt.
2. **Complexometric reaction:** This reaction involves the formation of a soluble complex between the metal ion and the complexing agent.
3. **Neutralization reaction:** This reaction involves the neutralization of an acid and a base.
4. **Redox reaction:** This reaction involves an oxidizing agent and a reducing agent.

The volumetric analysis is based on the following:

1. **Law of chemical equivalence:** This law states that substances react with each other in a definite ratio by mass. At a particular point called end-point, the number of gram equivalents of the reacting substances becomes equal.

Number of gram equivalents of substance 1 = Number of gram equivalents of substance 2

2. **Normality equation:** The law of chemical equivalence can be expressed in terms of normality of the two reacting substances:

$$N_1V_1 = N_2V_2$$

where N_1 and N_2 are normalities of substances 1 and 2 and V_1 and V_2 are the volumes of substances 1 and 2, respectively. This is known as the normality equation. If N_1, V_1 and V_2 are known, then N_2 and thus the unknown strength can be calculated.

Some Terms Used in Volumetric Analysis

The following terms are used in volumetric analysis:

1. **Titrant:** The standard solution of accurately known strength.
2. **Titrate:** The solution containing the substance whose concentration/strength is to be determined.
3. **Equivalence point:** The exact or theoretical point at which the reaction is complete.
4. **End-point:** The point, practically observed, at which a physical change is observed near the equivalence point.
5. **Indicator:** The substance used for visual detection (by color change) on completion of reaction at the end-point. A good indicator must have the following characteristics:
   (a) It must be sensitive at the equivalence point and the color change at the end point must be clear and sharp.
   (b) The pH range of the indicator should be such that the reaction gets completed within that range.
6. **Types of indicators:** The following types of indicators are used in volumetric analysis:
   (a) **Acid-base indicators:** Indicators which have different color in acid and alkaline solutions.

   Since the process of acid–base titration is accompanied by a change in pH and the equivalence point occurs at a definite pH value, indicators which change color in accordance with pH are used to indicate the end-point. These indicators have one color in acidic solution and another in alkaline solution.
   Different indicators have different pH ranges within which they can be used. For example,
   - methyl orange is pink in acidic medium and yellow in basic medium and works within 3.1–4.4 pH range;
   - phenolphthalein is colorless in acidic medium and pink in basic medium and works within 8.0–9.6 pH range and
   - methyl red is red in acidic medium and yellow in basic medium and works within 4.5–6.5 pH range.

   (b) **Redox indicators:** Indicators whose oxidized form has a color different from that of the reduced form.
   (c) **Precipitation indicators:** Indicators which are used for the formation of colored precipitates.
   (d) **Complexometric indicators:** Indicators which undergo a change in color on forming complex with metals.
7. **Parts per million (ppm):** Parts per million denotes the amount of a substance per 1,000,000 or 10^6 parts of the solution regardless of the units of measure used as long as they are same.
8. **Standard solution:** The solution of accurately known concentration used for determining the strength of solutions of unknown concentrations by titration. It can be classified into two types:
   (a) **Primary standard solution:** The solution that can be prepared directly by dissolving an accurately weighed amount of the substance in water and making up the volume to a known amount by water. Its concentration is mostly expressed in mol L^{-1} or mol dm^{-3}.

   The substance used for preparing standard solution should be available in highly pure state and should possess a high equivalent weight to minimize error while weighing. It should not be hygroscopic or efflorescent and should be stable for drying at oven temperature. Its composition should not be affected by air during storage and it should be readily soluble in water or any desired solvent. Examples of primary standards include: Oxalic acid, $AgNO_3$, KCl, anhydrous Na_2CO_3, etc.

   (b) **Secondary standard solution:** The solution that cannot be prepared by directly weighing the standard substance and dissolving it in water. These substances do not possess the properties of primary standard substances. In preparation of secondary standard solution, an approximate weight of such a substance is dissolved in water and then the strength of this solution is determined by titrating against a primary standard solution. This process is known as standardization. Examples of secondary standard solutions include: NaOH, $KMnO_4$, HCl, etc.

2.8 | TYPES OF TITRATIONS

Redox Titrations

Redox titration or oxidation–reduction titration can be defined as the titrations involving a reducing agent and an oxidizing agent. Since oxidation and reduction occur simultaneously and are complimentary to each other, such reactions are termed as redox reactions. For example,

$$\underset{\substack{\text{(Oxidizing}\\ \text{agent)}}}{\mathrm{MnO_4^-}} + \underset{\substack{\text{(Reducing}\\ \text{agent)}}}{\mathrm{5Fe^{2+}}} + 8\mathrm{H^+} \rightarrow \mathrm{Mn^{2+}} + 5\mathrm{Fe^{3+}} + 4\mathrm{H_2O}$$

Common oxidizing agents used in volumetric analysis are $KMnO_4$, $K_2Cr_2O_7$, KI, KBr, iodine, etc.

Redox Indicators

Any indicator whose oxidized and reduced forms differ in color and whose oxidation and reduction is readily reversible can be termed as a redox indicator. The quantitative relationship between reactants and products in case of redox reactions are calculated similarly as in case of general chemical reactions. The first mandatory step is to write a balanced chemical equation for the redox reaction. The coefficient of the reductant and oxidant will tell us the exact number of moles of each taking part in the redox reaction. If the stoichiometric coefficients of the reductant and oxidant are n_1 and n_2, respectively, then in a volumetric estimation, the molarity equation may be written as

$$\frac{M_1V_1}{n_1} = \frac{M_2V_2}{n_2}$$

The equation can be used for the calculation of any one variable out of the four, if the other three are known.

The change in color of a redox indicator is dependent upon the electrode potential of the system. Redox indicators are of three types:

1. **Self-indicator:** If the reacting solution changes color on reacting with the titrate, it is termed as self-indicator. In this case, no other indicator is added to determine the end-point. For example, $KMnO_4$ is purple in oxidized form but colorless in reduced form. When titrated with a reducing agent (e.g., oxalic acid or Mohr's salt), it becomes colorless. After all the reducing agent is consumed, addition of an excess drop of $KMnO_4$ solution gives a pink color to the solution indicating the end-point.
2. **Internal indicator:** Any indicator which is added to the volumetric flask in which the titration is carried out is called internal indicator. For example, diphenylamine is added in the titration of Fe (II) with $K_2Cr_2O_7$. After all the Fe (II) is consumed, addition of an excess drop of $K_2Cr_2O_7$ oxidizes diphenylamine which gives a violet color to the solution indicating the end-point.
3. **External indicator:** An indicator that cannot be added to the volumetric flask in which the titration is carried out but can be used externally is called *external indicator*. Drops of external indicator are placed on a tile by a dropper. As the titration proceeds, drops of reaction mixture are taken out by a glass rod and tested by mixing with the drops of indicator on the tile. Color change of the indicator marks the end-point. This is a rough estimation as a number of drops of the reaction mixture are taken out from the volumetric flask. For example, $K_3Fe(CN)_6$ is used as an indicator in the titration of $K_2Cr_2O_7$ with ferrous ammonium sulphate. It gives blue color on reaction with Fe^{2+} ions due to the formation of $Fe_3[Fe(CN)_6]_2$. When all Fe^{2+} is converted to Fe^{3+}, blue color is no longer obtained.

Potassium Permanganate Titrations

Potassium permanganate is a strong oxidizing agent in both acidic as well as basic medium. Generally, $KMnO_4$ titration in acidic medium proceeds according to the following reaction:

$$\mathrm{MnO_4^-} + 8\mathrm{H^+} + 5e^- \rightarrow \mathrm{Mn^{2+}} + 4\mathrm{H_2O}$$

For acidification, H_2SO_4 is generally used. Use of HCl is avoided as $KMnO_4$ oxidizes HCl to Cl_2 gas. HNO_3 is not used as it is itself a strong oxidizing agent and thus itself may oxidize the reducing agent.

Potassium permanganate is used in the estimation of reducing agents like oxalic acid according to the reaction:

$$2KMnO_4 + 3H_2SO_4 + 5H_2C_2O_4 \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2$$

No indicator is used in this titration as $KMnO_4$ acts as self-indicator. The drawback with $KMnO_4$ titration is that it is not a primary standard and has to be standardized before using.

Potassium Dichromate Titrations

Potassium dichromate acts as an oxidizing agent only in acidic medium according to the following reaction:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow Cr^{3+} + 7H_2O$$

For acidification both H_2SO_4 and HCl can be used as $K_2Cr_2O_7$ does not oxidize HCl at room temperature. In estimation of iron in Mohr's salt, $[(NH_4)_2Fe(SO_4)_2\ 6H_2O]$ $K_2Cr_2O_7$ oxidizes $FeSO_4$ to $Fe_2(SO_4)_3$ in the presence of dilute H_2SO_4 as illustrated in the following reaction:

$$Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

Diphenylamine is used as an internal indicator. It oxidizes from colorless to blue color by oxidation with $Cr_2O_7^{2-}$ at the end-point. $K_2Cr_2O_7$ is less powerful oxidizing agent than $KMnO_4$ but the advantage is that it is a primary standard.

Iodine Titrations

Iodine is a mild oxidizing agent. It acts as an oxidizing agent in neutral aqueous medium as per the following reaction:

$$I_2 + 2e^- \rightarrow 2I^-$$

On the other hand, $2I^-$ can be oxidized to I_2 in the presence of an oxidizing agent. Indicator used in iodine titrations is starch. It gives blue color at the end-point. Iodine titrations can be classified as:

1. **Iodometry:** Titrations in which iodine liberated during the oxidation of iodide ions by strong oxidizing agent, is titrated with a reducing agent and the strength of the oxidizing agent is estimated are called *iodometric titrations*. For example, estimation of Cu^{2+} with thiosulphate involving the following reactions:

$$2Cu^{2+} + \underset{\substack{\text{Oxidizing}\\ \text{agent}}}{4I^-} \rightarrow Cu_2I_2 + I_2$$

$$\underset{\substack{\text{Reducing}\\ \text{agent}}}{I_2} + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2I^-$$

   In the first step, Cu^{2+} is reduced to Cu^+ by the addition of potassium iodide in excess in the pH range 4.0–5.5. The iodine liberated is titrated against sodium thiosulphate using starch as indicator. The estimated amount of iodine is stoichiometrically equal to the amount of copper present.
2. **Iodimetry:** Titrations involving the direct titration of iodine with a reducing agent are termed as iodimetric titrations. Examples of iodimetric titration include the determination of strength of ferrous ions, sulphite ions, arsenite ions and thiosulphate ions.

Solved Example 2-36

1.0 g of a sample of H_2O_2 solution containing $y\%$ H_2O_2 by weight requires y mL of $KMnO_4$ solution for complete titration under acidic condition. Find the molarity of $KMnO_4$ solution.

Solution

This involves a redox reaction between H_2O_2 (reducing agent) and $KMnO_4$ (oxidizing agent). Applying the concept of gram (milli) equivalents, we have

$$\text{Milliequiv. of } H_2O_2 = \text{Milliequiv. of } KMnO_4$$

Let us find valence factor (i.e., number of electrons involved in redox reactions) of H_2O_2 and $KMnO_4$ from the half reactions:

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

and $$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$$

Now, the electrons involved = 5 for $KMnO_4$ and 2 for H_2O_2. Therefore,

$$\text{Milliequiv. of } H_2O_2 = \frac{1 \times \left(\dfrac{y}{100}\right)}{\text{Equivalent weight}} \times 1000$$

where equivalent weight of $H_2O_2 = 34/2$. Now,

$$\text{Milliequiv. of } KMnO_4 = N(y) = \frac{1 \times \left(\dfrac{y}{100}\right)}{34/2} \times 1000 \Rightarrow N = \frac{10}{17}$$

$$\text{Molarity} = \frac{\text{Normality}}{5} = \frac{10/17}{5} = \frac{2}{17} = 0.117 \text{ M}$$

Solved Example 2-37

A sample of Pyrolusite (MnO_2) weighs 0.5 g. To this solution 0.594 g of As_2O_3 and a dil acid are added. After the reaction has stopped, As^{3+} in As_2O_3 is titrated with 45 mL of M/50 $KMnO_4$ solution. Calculate the percentage of MnO_2 in pyrolusite.

Solution

The reaction involved is

$$\underset{0.5\text{ g}}{MnO_2} + \underset{0.594\text{ g}}{As_2O_3} \rightarrow Mn^{2+} + AsO_4^{3-}$$

For excess of As_2O_3, we have

$$As_2O_3 + MnO_4^- \rightarrow Mn^{2+} + AsO_4^{3-}$$

Now, As_2O_3 is getting oxidized to AsO_4^{3-}, the half reaction is

$$As_2O_3 + 5H_2O \rightarrow 2As + 10H^+ + 4e^-$$

For 1 mol of As_2O_3, number of electrons = 4. So, equivalent weight of $As_2O_3 = 198/4$

$$\text{Milliequiv. of } As_2O_3 \text{ taken} = \frac{0.594}{198/4} \times 1000 = 12$$

Milliequiv. of excess As_2O_3 = milliequiv. of $KMnO_4$ = $45[1/50 \times 5] = 4.5$.
The other half reaction is

$$MnO_4^- + 5e^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O$$

Note that the number of electron transfer for As_2O_3, in the two reactions is the same. So milliequiv. of As_2O_3 used for $MnO_2 = 12 - 4.5 = 7.5$

Now, milliequiv. of MnO_2 = 7.5. Therefore, the grams of MnO_2 is

$$\frac{w}{87/2} \times 1000 = 7.5 \Rightarrow w = 0.326 \text{ g}$$

For the half reaction $MnO_2 + 4H^+ \rightarrow Mn^{2+} + 2e^- + 2H_2O$. Therefore, the percentage of MnO_2 present is

$$\%MnO_2 = \frac{0.326}{0.5} \times 100 = 65.25\%$$

Solved Example 2-38

0.5 g sample containing MnO_2 is treated with HCl, liberating Cl_2. The Cl_2 is passed into a solution of KI and 30.0 cm^3 of 0.1 M $Na_2S_2O_3$ are required to titrate the liberated iodine. Calculate the percentage of MnO_2 in sample (atomic weight of Mn = 55).

Solution

The half reactions are

$$2e^- + I_2^0 \rightarrow 2I^-$$
$$2S_2^{2+} \rightarrow S_4^{(5/2)^+} + 2e^-$$
$$2e^- + Mn^{4+} \rightarrow Mn^{2+}$$

From the reactions, we have

Milliequiv. of MnO_2 = Milliequiv. of Cl_2 formed = Milliequiv. of I_2 liberated = Milliequiv. of $Na_2S_2O_3$ used

Now, since from the reactions we have valency factor for $Na_2S_2O_3 = 1$, so $N_{Na_2S_2O_3} = M_{Na_2S_2O_3}$.

$$\text{Therefore, } \frac{\text{Weight}}{\text{Equivalent weight}} \times 1000 = 0.1 \times 1 \times 30$$

or

$$w_{MnO_2} = \frac{0.1 \times 1 \times 30 \times M_{B(MnO_2)}}{2000} = \frac{0.1 \times 1 \times 30 \times 87}{2000} = 0.1305 \text{ g}$$

$$\text{Hence, \%purity of } MnO_2 = \frac{0.1305}{0.5} \times 100 = 26.1\%$$

Complexometric Titrations

Complexometric titrations refer to those titrations which are based on the formation of a soluble complex between the metal ion and the complexing agent (ligand). These titrations are generally used for the estimation of calcium and magnesium by ethylenediamine tetraacetic acid (EDTA).

Selection of Indicators

Indicator for complexometric titration is selected such that it forms a less stable complex with metal atom than the metal–ligand complex and releases the metal ion at equivalence point resulting in a color change, thus indicating the end-point.

Most widely used indicator is Eriochrome Black T (EBT). It is known as metal ion indicator because it forms intensely colored complexes with metal ions which are visible to the eye even at low temperatures. The free indicator has a color different from the metal complex and hence the release of free indicator marks the end-point. EBT exhibits different colors in different pH ranges. So the pH of the solution is maintained by a suitable buffer for appearance of blue color to mark the end-point.

Estimation of Hardness of Water by EDTA Method

Hardness of water can be defined as its capacity to precipitate soap. It is due to the presence of calcium and magnesium salts. Hardness of water is of two types:

Hardness is classified into temporary hardness and permanent hardness.

1. **Temporary hardness:** This hardness results in water that contains bicarbonates of calcium and magnesium. It can be removed by boiling. The bicarbonates decompose on boiling giving rise to carbonates and hydroxides which are insoluble and deposit at the bottom of the vessel.

$$Ca(HCO_3)_2 \xrightarrow{\Delta} CaCO_3\downarrow + H_2O + CO_2$$
$$Mg(HCO_3)_2 \xrightarrow{\Delta} Mg(OH)_2\downarrow + 2CO_2$$

   This hardness is also known as carbonate or alkaline hardness. To determine the temporary hardness, a given volume of hard water is titrated with a strong acid (HCl or H_2SO_4) using methyl orange indicator.

2. **Permanent hardness:** This hardness is due to presence of chlorides and sulphates of calcium and magnesium in water. Thus, it can be caused mainly by the presence of salts such as $MgCl_2$, $MgSO_4$, $CaCl_2$ and $CaSO_4$ and also salts of heavier elements such as iron and aluminium. This type of hardness cannot be removed by boiling but can be removed by the addition of softening agents.

The various units used to express hardness of water are as follows:

1. **Parts per million (ppm):** It is the number of equivalent parts of $CaCO_3$ present per million (10^6) parts of water by weight.
2. **Milligrams per liter:** It is the number of mg of $CaCO_3$ dissolved in 1 L of water. We know that 1 L of water weighs 1 kg $= 1000 \times 1000 = 10^6$ mg

   So, 1 mg L^{-1} = 1 mg of $CaCO_3$ per 10^6 mg of water = 1 part of $CaCO_3$ per 10^6 parts of water = 1 ppm
3. **Degree Clarke (°Cl):** It is the number of equivalent parts of $CaCO_3$ present per 70,000 parts of water or 1 gallon of water.
4. **Degree French (°Fr):** It is the number of equivalent parts of $CaCO_3$ present per 10^5 parts of water.

These various units of hardness are related as: 1 ppm = 1 mg/l = 0.1°Fr = 0.07°Cl

Estimation of hardness of water can be carried out by complexometric titration using EDTA as complexing agent and EBT as indicator. EBT when added to water forms an unstable wine-red colored complex with calcium and magnesium. As the solution is titrated with EDTA, free Mg^{2+} and Ca^{2+} present in water form stable colorless complex with EDTA. Once all the free Mg^{2+} and Ca^{2+} are complexed, EDTA replaces Mg^{2+} and Ca^{2+} complexed with EBT in the unstable wine-red complex. Free EBT imparts blue indicating the end-point of the reaction. The amount of EDTA used in the titration corresponds directly to the hardness of water.

$$Mg^{2+}/Ca^{2+} + EBT \rightarrow \underset{\text{(Unstable wine-red complex)}}{[Mg/Ca\text{–}EBT]}$$

$$Mg^{2+}/Ca^{2+} + EDTA \rightarrow \underset{\text{(Stable colorless complex)}}{[Mg/Ca\text{–}EDTA]}$$

$$[Mg/Ca - EBT] + EDTA \rightarrow \underset{\text{(Blue color)}}{[Mg/Ca\text{–}EDTA] + EBT}$$

Clarke's method is used for removal of temporary hardness of water. The reactions involved are

$$Ca(OH)_2 + Ca(HCO_3)_2 \rightarrow 2CaCO_3 + 2H_2O$$
$$Ca(OH)_2 + Mg(HCO_3)_2 \rightarrow MgCO_3 + CaCO_3 + 2H_2O$$

Solved Example 2-39

A particular water sample is found to certain 96.0 ppm of SO_4^{2-} and 122.0 ppm of HCO_3^-, with Ca^{2+} as the only cation.

(a) How many ppm of Ca^{2+} does this water contain?

(b) How many mol of CaO are consumed in removing HCO_3^- from 1.00×10^6 g of the water described above?

(c) What is the concentration of Ca^{2+} remaining in the water after the treatment above?

Solution

(a) The reactions involved are

$$CaSO_4 \rightleftharpoons Ca^{2+} + SO_4^{2-}$$

$$Ca(HCO_3)_2 \rightleftharpoons Ca^{2+} + 2HCO_3^-$$

Every mole of $CaSO_4$ has one mole each of Ca^{2+} and SO_4^{2-} but every mol of $Ca(HCO_3)_2$ has one mole of Ca^{2+} half the mole of HCO_3^-. Therefore, we have

96 ppm = 96 g SO_4^{2-} in 10^6 mL H_2O (1000 L as ppm is mg L^{-1}) = 1.0 mL of SO_4^{2-} = 1.0 mol of Ca^{2+}

122 ppm = 122 g HCO_3^- in 10^6 mL H_2O = 2.0 mol of HCO_3^- = 1.0 mol of Ca^{2+}

Total grams of Ca^{2+} present = 1 + 1 = 2.0 mol of Ca^{2+} = 80 g in 10^6 mL H_2O. Therefore, Ca^{2+} = 80 ppm.

(b) $CaO + Ca(HCO_3)_2 \rightarrow 2CaCO_3 + H_2O$ (Clarke's method)

1 mol of $Ca(HCO_3)_2$ requires = 1 mol of CaO ≡ 2 mol HCO_3^- = 1.0 mol of CaO

(c) In part **(b)**, by adding CaO, HCO_3^- is removed as $CaCO_3$. Thus SO_4^{2-} is left. The moles of HCO_3^- removed = 2.0 mol.

Hence, Ca^{2+} removed = 1.0 mol
Now, total Ca^{2+} already present = 2.0 mol
Hence, Ca^{2+} left = 2.0 – 1.0 = 1.0 mol = 40 g. Thus Ca^{2+} left in water = 40 ppm.

Precipitation Titrations

Precipitation titrations are defined as the titrations involving the formation of a sparingly soluble salt by the reaction of titrate and titrant. Precipitation occurs only when the ionic product exceeds the solubility product. Indicator used in these titrations works on the principle of formation of a colored complex. Important criteria for precipitation titration are that the formation of precipitate should be fast and the precipitate formed must be insoluble.

Argentometric Titration

The most workable precipitation titrations for volumetric analysis are those involving $AgNO_3$ and hence called argentometric titrations. The indicators used in these titrations may involve formation of colored precipitate or a soluble colored compound, based on which, the two important argentometric titrations involved are Mohr's method and Volhard's method, respectively. These are described as follows:

1. **Mohr's method:** This method, for the estimation of chlorides, involves the titration of $AgNO_3$ against halides in neutral medium using K_2CrO_4 as indicator.

$$Ag^+ + Cl^- \rightarrow \underset{\text{(White precipitate)}}{AgCl}$$

$$2Ag^+ + \underset{\text{(Indicator)}}{CrO_4^{2-}} \rightarrow \underset{\text{(Brick-red precipitate)}}{Ag_2CrO_4}$$

Formation of brick-red precipitate of Ag_2CrO_4 marks the end-point. Ag_2CrO_4 is formed only after the complete precipitation of AgCl as the solubility product of AgCl is reached earlier than that of Ag_2CrO_4.

Note:

1. Neutral medium is very important as Ag_2CrO_4 is soluble in acidic medium and $AgNO_3$ is precipitated as AgOH in alkaline medium.
2. This method is used for the estimation of chlorides only. It may not be used for estimation of iodides, because the precipitates formed by iodides would mask the color of the indicator.

2. **Volhard's method:** This method, for the estimation of silver, involves the titration of $AgNO_3$ against ammonium or potassium thiocyanate in the presence of dilute HNO_3 using ferric salt as indicator.

$$Ag^+ + SCN^- \rightarrow \underset{\text{(White precipitate)}}{AgSCN}$$

$$Fe^{3+} + \underset{\text{(Indicator)}}{SCN^-} \rightarrow \underset{\text{(Red precipitate)}}{Fe(SCN)_3}$$

Appearance of a red precipitate of $Fe(SCN)_3$ indicates the end-point. $Fe(SCN)_3$ is formed only after the complete precipitation of silver. This method can also be used for the estimation of bromides. However, it cannot be used for the estimation of chlorides as the precipitates formed by chlorides disappear on stirring.

Solved Example 2-40

A mixture containing only Na_2CO_3 weighing 1.22 g was dissolved in water to form 100 mL of a solution; 20 mL of this solution required 40 mL of 0.1 N HCl for neutralization.

(a) Calculate the weight of K_2CO_3 in the mixture.

(b) If another 20 mL of the same solution is treated with excess of $BaCl_2$, what will be the weight of precipitate thus obtained? (Molecular masses of $Na_2CO_2 = 106$, $K_2CO_3 = 138$, $BaCO_3 = 197.4$.)

Solution

(a) As both K_2CO_3 and Na_2CO_3 are bases, hence both of them will react with HCl. Given that for this experiment, 20 mL sample is taken from 100 mL of the solution.

Let x = mass of Na_2CO_3 be present in the 100 mL solution, then $1.22 - x$ = mass of K_2CO_3 in the solution. Now,

Mass of Na_2CO_3 in 20 mL of the sample $= \frac{x}{5}$ and mass of K_2CO_3 in the sample $= \frac{1.22 - x}{5}$.

At the end point, milliequiv. of mixture = milliequiv. of HCl, so

$$\left[\frac{x/5}{106/2} + \frac{(1.22 - x)/5}{138/2}\right] \times 1000 = 0.1 \times 40$$

$$69x - 53x + 1.22 \times 53 = \frac{0.1 \times 40 \times 5 \times 69 \times 53}{1000}$$

$$16x = 73.140 - 64.66$$

$$= 8.48$$

$$\Rightarrow x = 0.53 \text{ g}$$

Therefore, weight of $Na_2CO_3 = 0.53$ g and weight of $K_2CO_3 = 1.22 - 0.53 = 0.69$ g.

(b) When 20 mL of sample is treated with $BaCl_2$, $BaCO_3$ is precipitated.

$$BaCl_2 + Na_2CO_2 \rightarrow BaCO_3 + 2NaCl$$

$$BaCl_2 + K_2CO_3 \rightarrow BaCO_3 + 2KCl$$

Mass of Na_2CO_3 in 20 mL = $x/5 = 0.53/5 = 0.106$ g and moles of $Na_2CO_3 = 0.106/106 = 1.0\times10^{-3}$ mol.
Mass of K_2CO_3 in 20 mL = $0.69/5 = 0.138$ g and moles of $K_2CO_3 = 0.138/138 = 1.0\times10^{-3}$ mol.
From stoichiometry of above reaction, we have:
Moles of $BaCO_3$ = Moles of Na_2CO_3 + Moles of $K_2CO_3 = 1.0\times10^{-3} + 1.0\times10^{-3} = 2.0\times10^{-3}$
or mass of $BaCO_3 = (2.0\times10^{-3})\times197.4 = 0.395$ g.

Neutralization Titrations

The titrations involving acid and alkali or in other words titrations involving reaction between H^+ and OH^- ions to form water are termed as neutralization titrations or acid–base titrations. At the equivalence point, the pH of solution will be less than or greater than 7 depending upon the strength of the acid and alkali.

When the strength of an unknown acid is determined by using a known base, the titration is termed as **acidimetry**, whereas when the strength of an unknown base is determined by using a known acid, the titration is termed as **alkalimetry**. During titration, pH of the solution keeps changing and at a definite pH, end-point is reached.

A plot of pH against the volume of the acid or base added is known as acid–base titration curve or pH titration curve. Acid–base titration curves are helpful in determination of equivalence point for a given acid and base pair experimentally.

A typical curve for the change of pH with volume of alkali added is depicted in Figure 1.10. In the beginning, pH changes very slowly followed by a sharp increase near the equivalence point even for a very small amount of alkali added. After the equivalence point, pH again changes very slowly (Fig. 2.5).

A pH titration curve is significant to determine the equivalence point as well as to select a suitable indicator that exhibits a distinct change in color at a pH close to the equivalence point. The selection of indicator for a titration is decided based on the:

1. pH range of the indicator.
2. pH change near the equivalence point.

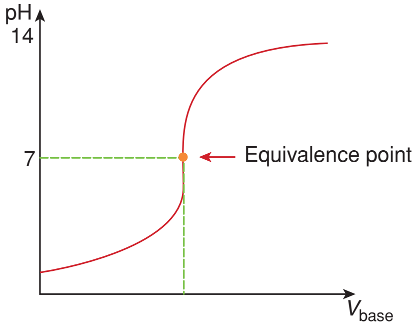


Figure 2.5 Acid–base (pH) titration curve.

An indicator with pH range included in the pH change of solution near the equivalence point is generally used. The pH range of some common indicators is given in Table 2.3.

Table 2.3 Common indicators and their pH range

		Color of indicator	
Indicator	pH range	Acidic medium	Basic medium
Phenolphthalein	8.3 to 10	Colorless	Pink
Methyl orange	3.1 to 4.4	Red	Orange
Methyl red	4.2 to 6.3	Red	Yellow
Litmus	5 to 8	Red	Blue

Different types of acid base titrations and indicators used in some important acid-base titrations are listed as follows:

1. **Strong acid-strong base titration:** In the titration of HCl with NaOH, the equivalence point lies in the range of 4 to 10, so phenolphthalein, methyl orange and methyl red can be used as indicators.
2. **Weak acid and strong base titration:** In the titration of acetic acid with NaOH, the equivalence point lies between 7.5 and 10, so phenolphthalein can be used as an indicator.

3. **Weak base and strong acid titration:** In the titration of NH_4OH with HCl, the pH equivalence point lies in the range of 4 to 6.5, so methyl orange and methyl red can be used as indicators.
4. **Weak acid and weak base titration:** In the titration of acetic acid with NH_4OH, the pH at equivalence point lies between 6.5 and 7.5 but no sharp change in pH is observed in these titrations. So no simple indicator can be used to identify the equivalence point.
5. **Titration of a salt of strong base and weak acid with strong base:** In the titration of sodium carbonate (salt of carbonic acid and sodium hydroxide), the neutralization reactions are:

$$Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$$
$$NaHCO_3 + HCl \rightarrow NaCl + H_2CO_3$$

In the first reaction, the equivalence point is near pH 8.3 and is near pH 4 for the second reaction. So the suitable indicator for the first reaction is phenolphthalein and methyl orange for the second reaction.

Solved Example 2-41

A small amount of $CaCO_3$ completely neutralizes 525 mL of 0.1 N HCl and no acid is left in the end. After converting all calcium chloride to $CaSO_4$, how much plaster of Paris can be obtained?

Solution

525 mL of 0.1 N HCl = 525 mL of 0.1 N $CaCl_2$ = 525 mL of 0.1 N plaster of Paris.

Molecular mass of plaster of Paris = 145 g

$$\text{Equivalent mass of plaster of Paris} = \frac{145}{2} = 72.5 \text{ g}$$

Mass of plaster of Paris in 525 mL of 0.1 N solution is

$$\frac{\text{Normality} \times \text{Equivalent mass} \times \text{Volume}}{1000} = \frac{0.1 \times 72.5 \times 525}{1000}$$
$$= 3.806 \text{ g}$$

Solved Example 2-42

In an attempt to establish the formula of an oxide of nitrogen, a known volume of the pure gas was mixed with hydrogen and passed over a catalyst at a suitable temperature. Conversion of the oxide to ammonia and water was to have taken place.

$$N_xO_y \xrightarrow{H_2(g),\text{ catalyst}} x\,NH_3 + y\,H_2O$$

2400 cm^3 of the nitrogen oxide, measured at room temperature and pressure produced 7.20 g of water. The ammonia produced was neutralized by 200 cm^3 of 1.0 mol dm^{-3} HCl. What is the oxidation number of the nitrogen in the nitrogen oxide?

Solution

The reaction involved is

$$\underset{\substack{2400\text{ cm}^3\\0.1\text{ mol}}}{N_xO_y} \xrightarrow{H_2(g),\text{ catalyst}} \underset{0.2\text{ mol}}{x\,NH_3} + \underset{0.4\text{ mol}}{y\,H_2O}$$

(24000 cm^3 = 1 mol at room condition = 298 K and 1 atm)

$$\text{Amount of } H_2O = \frac{7.20}{18} = 0.40 \text{ mol}$$

$$NH_3(aq) + HCl(aq) \rightarrow NH_4^+(aq) + Cl^-(aq)$$

$$\text{Number of moles of HCl} = \frac{1}{1000} \times 200 = 0.2 \text{ mol}$$

$$\text{Number of moles of } NH_3 = 0.2 \text{ mol}$$

0.1 mol of N_xO_y produces 0.2 mol of NH_3 and 0.4 mol of H_2O

1 mol of N_xO_y produces 2 mol of NH_3 and 4 mol of H_2O

$$\underset{1\text{ mol}}{N_xO_y} \rightarrow \underset{2\text{ mol}}{x\,NH_3} + \underset{4\text{ mol}}{y\,H_2O}$$

where $x = 2, y = 4$. Formula of nitrogen oxide is N_2O_4.

Oxidation state of N in N_2O_4 is: $2x + 4(-2) = 0 \Rightarrow 2x - 2 = 0 \Rightarrow x = +4$.

Solved Example 2-43

5 mL of 8 N HNO_3, 4.8 mL of 5 N HCl and a certain volume of 17 M H_2SO_4 are mixed together and made upto 2 L. 30 mL of the acid mixture exactly neutralized by 42.9 mL of Na_2CO_3 solution containing 0.1 g of $Na_2CO_3 \cdot 10H_2O$ in 10 mL of water. Calculate **(a)** the volume of H_2SO_4 added to the mixture and **(b)** the amount (in gram) of the sulphate ions in the solution.

Solution

(a) We know that milliequiv. of acid mixture = milliequiv. of HNO_3 + milliequiv. of HCl + milliequiv. of H_2SO_4.

Let N be the normality of the acid mixture and V_1 be the volume of H_2SO_4 added. We have

$$N \times 2000 = 8 \times 5 + 4.8 + 2(17) \times V_1 \qquad (1)$$

Now, we find the normality of carbonate as follows:

Amount of $Na_2CO_3 \cdot 10H_2O$ used = 42. mL × $\frac{0.1\text{ g}}{10\text{ mL}} = 0.429$ g

The number of moles of $Na_2CO_3 \cdot 10H_2O = \frac{0.429}{286} =$ 0.0015 mol

The number of moles of acid reacting with those of $Na_2CO_3 \cdot 10H_2O$ are as follows:

1 mol of $Na_2CO_3 \cdot 10H_2O$ reacts with 2 mol of acid, so

0.0015 mol of $Na_2CO_3 \cdot 10H_2O$ will react with 0.003 mol of acid.

Now, for $Na_2CO_3 \cdot 10H_2O$ we have normality = molarity × 2 = $\frac{0.0015}{42.9} \times 1000 \times 2 = 0.069$ N

From the relation N × V (acid mixture) = $N_2 \times V_2$ ($Na_2CO_3 \cdot 10H_2O$), we have

$$N = \frac{0.07 \times 42.9}{30} = 0.1\text{ N}$$

Substituting in Eq. (1), we get

$$0.1 \times 2000 = 40 + 24 + 34 \times V_1 \Rightarrow V_1 = 4\text{ mL}$$

(b) For grams of sulphate ion, we have

Milliequiv. of $H_2SO_4 = 2 \times 17 \times V_1 = 136$

Now, milliequiv. of SO_4^{2-} = milliequiv. of H_2SO_4

Grams of sulphate ion can be found as

$$\frac{\text{Weight}}{\text{Equivalent weight}} \times 1000 = 136$$

$$\Rightarrow \text{Weight} = 136 \times \frac{96}{2} \times \frac{1}{1000} = 6.528\text{ g}$$

Solved Example 2-44

The neutralization of a solution of 1.2 g of mixture of $H_2C_2O_4 \cdot 2H_2O$ and $KHC_2O_4 \times H_2O$ and some impurities which are neutral, consumed 40.0 mL 0.25 N NaOH. On the other hand, on titration with $KMnO_4$, a 0.4 g of mixture required 40.0 mL of 0.125 N $KMnO_4$. Find the percentage composition of mixture.

Solution

Note that the mass of two samples is different in two titrations.

Let x = moles of $H_2C_2O_4 \cdot 2H_2O$ and y = moles of $KHC_2O_4 \cdot H_2O$ in 0.4 g sample.

So, moles of oxalic acid in 1.2 g sample = $3x$ and moles of bioxalate in 1.2 g sample = $3y$

Neutralization with NaOH:

Milliequiv. of $H_2C_2O_4 \cdot 2H_2O$ + Milliequiv. of $KHC_2O_4 \cdot H_2O$ = Milliequiv. of NaOH

Since acid has $2H^+$ ions whereas bioxalate has only 1 H^+, we have

$$2 \times 3x + 1 \times 3y = 0.25 \times 40 \Rightarrow 2x + y = \frac{10}{3}$$

Redox reaction with $KMnO_4$:

Milliequiv. of $H_2C_2O_4 \cdot 2H_2O$ + Milliequiv. of $KHC_2O_4 \cdot H_2O$ = Milliequiv. of $KMnO_4$

Now, we have the reactions

$$HC_2O_4^- \rightarrow 2CO_2 + H^+ + 2e^-$$
$$C_2O_4^{2-} \rightarrow 2CO_2 + H^+ + 2e^-$$

Thus, we have $2 \times x + 2 \times y = 0.125 \times 40 \Rightarrow x + y = 2.5$

Solve for x and y, we get $x = 5/6$ and $y = 5/3$.

Now, $x = \frac{g_{H_2C_2O_4 \cdot 2H_2O}}{M_{H_2C_2O_4 \cdot 2H_2O}} \times 1000 = \frac{5}{6}$ and

$$y = \frac{g_{KHC_2O_4 \cdot 2H_2O}}{M_{KHC_2O_4 \cdot 2H_2O}} \times 1000 = \frac{5}{3}$$

Substituting $M_{B(H_2C_2O_4 \cdot 2H_2O)} = 126$ and $M_{B(KHC_2O_4 \cdot 2H_2O)} =$ 144, we get

$$g_{H_2C_2O_4 .2H_2O} = 0.105\text{ g and } g_{KHC_2O_4 .2H_2O} = 0.243\text{ g}$$

Therefore, the percentage composition of the mixture is

$$\%H_2C_2O_4 \cdot 2H_2O = \frac{0.105}{0.4} \times 100 = 26.25\% \quad \text{and}$$

$$\%\ KHC_2O_4 \times H_2O = \frac{0.243}{0.4} \times 100 = 60.75\%$$

Double Titration

If an aqueous solution contains a mixture of any two of the three NaOH, $NaHCO_3$ and Na_2CO_3 and it has to be titrated against an acid HCl or H_2SO_4, it will require two indicators to determine the strength of the bases present. The two indicators used are phenophthalein and methyl orange.

Method: A given volume of the aqueous solution of the bases is taken and phenolphthalein indicator is added to it. This solution is titrated with an acid of known normality to the end point the volume of the acid used is noted. This end point is called first end point. Now in the same solution, methyl orange is added and gain titrated with an acid of known strength to the end point. It is called second end point. The volume of acid, used in the second end point is also noted. The normality of the bases present is then calculated.

Principle: In the presence of phenolphthalein indicator

1. NaOH is completely neutralized by the acid.
2. Only half of the milliequivalents of Na_2CO_3 present are titrated as the phenolphthalein will show the color change when only $NaHCO_3$ (weak base) and neutral species are left in the reaction mixture. The following reactions take place,

$$NaOH + HCl \rightarrow NaCl + H_2O$$
$$Na_2CO_3 + HCl \rightarrow \underset{\text{weak base}}{NaHCO_3} + NaCl$$

Since phenolphthalein is a weak organic acid, and it changes its color in weakly basic medium ($NaHCO_3$), so as soon as the Na_2CO_3 is converted to $NaHCO_3$ phenolphthalein shows the color change indicating the completion of the reaction.

In the presence of methyl orange, all the basic substances left in the mixture will be neutralized by acid and methyl orange will show the color change when the medium is weakly acidic ($H_2O + CO_2$, that is, H_2CO_3)

Applications:

1. **Titration of the solution containing both NaOH and Na_2CO_3:** A given volume of the aqueous solution is titrated with an acid of known normality using phenolphthalein indicator. Suppose *a* milliequivalents of acid are used in the first end point then,

$$\text{Milliequivalent of NaOH} + 1/2 \times \text{Milliequivalent of } Na_2CO_3 = \text{Milliequivalent of acid} = a \qquad (2.2)$$

Now, in the same already titrated solution, methyl orange indicator is added and again titrated to the end point. Suppose *b* milliequivalents of the acid are used at the second end point, then

$$1/2 \times \text{Milliequivalents of } Na_2CO_3 = \text{Milliequivalents of acid} = b \qquad (2.3)$$

From Eqs. (2.2) and (2.3)

$$\text{Milliequivalents of acid used by } Na_2CO_3 = 2b \equiv \text{Milliequivalents of } Na_2CO_3$$
$$\text{Milliequivalents of acid used by NaOH} = a - b = \text{Milliequivalent of NaOH}$$

Knowing the milliequivalents of Na_2CO_3 or NaOH and the volume of the solution titrated, their normality can be calculated.

Solved Example 2-45

NaOH and Na_2CO_3 are dissolved in 200 mL aqueous solution. In the presence of phenolphthalein indicator, 17.5 mL of 0.1 N HCl are used to titrate this solution. Now methyl orange is added in the same solution titrated and it requires 2.5 mL of the same HCl. Calculate the normality of NaOH and Na_2CO_3 and their mass present in the solution.

Solution

Milliequivalents (*a*) of HCl used in the presence of phenolphthalein indicator = $N \times V$ (mL) = $0.1 \times 17.5 = 1.75$

$$1.75(a) = \text{Milliequiv. of NaOH} + \frac{1}{2} \times \text{Milliequiv. of } Na_2CO_3 \qquad (1)$$

Milliequivalents (b) of HCl used in the presence of methyl orange indicator = $N \times V$ (mL) = $0.1 \times 2.5 = 0.25$.

$$0.25(b) = \frac{1}{2} \times \text{Milliequiv. of Na}_2\text{CO}_3 \tag{2}$$

For Na_2CO_3 solution: From Eq. (2), we have
Milliequiv. of acid used by $Na_2CO_3 = 2b = 2 \times 0.25 = 0.5$
Volume of Na_2CO_3 solution = 200 mL
Suppose normality of Na_2CO_3 = N_1 then milliequiv. of $Na_2CO_3 = N_1 \times V_1$ (mL) = 200 N
Setting equivalents of acid and Na_2CO_3 equal, we get 200 $N_1 = 0.5$. Now,

$$\text{Mass of Na}_2\text{CO}_3 = N_1 \times \text{Equivalent weight} \times V_1(\text{L})$$

where equivalent weight for Na_2CO_3 = 106/2 = 53. Substituting, we get

$$\text{Mass of Na}_2\text{CO}_3 = \frac{0.5}{200} \times 53 \times 0.2 = 0.0265 \text{ g}$$

For NaOH solution: From Eqs. (1) and (2), we get

Milliequiv. of acid used by NaOH = $a - b = 1.75 - 0.25 = 1.50$

Given that volume of NaOH solution = 200 mL. Now, suppose normality of NaOH solution = N_2, we have

$$\text{Milliequiv. of NaOH} = N_2 \times V_2(\text{mL}) = 200 \text{ N}$$

Setting the milliequiv. of NaOH and acid used equal, we get $200\ N_2 = 1.5 \Rightarrow N_2 = \dfrac{1.5}{200}$

Therefore, mass of NaOH = $N_2 \times$ Equivalent weight $\times$ $V_2\ (\text{L}) = \dfrac{1.5}{200} \times 40 \times 0.2 = 0.06$ g

---

2. **Titration of the solution containing both Na_2CO_3 and $NaHCO_3$:** Given volume of the solution is titrated by an acid using phenolphthalein indicator. Suppose a milliequivalents of acid are used in the first end point, then,

$$\frac{1}{2} \times \text{Milliequiv. of Na}_2\text{CO}_3 = \text{Milliequiv. of acid} = a \tag{2.4}$$

Now in the same already titrated solution, methyl orange indicator is added and again titrated to the end point. Suppose b milliequivalents of the acid are used at the second end point, then,

$$\frac{1}{2} \times \text{Milliequiv. of Na}_2\text{CO}_3 + \text{Milliequiv. of NaHCO}_3 = \text{Milliequiv. of acid} = b \tag{2.5}$$

From Eqs. (2.4) and (2.5), we have

$$\text{Milliequiv. of acid used by Na}_2\text{CO}_3 = 2a \equiv \text{Milliequiv. of Na}_2\text{CO}_3$$

$$\text{Milliequiv. of acid used by NaHCO}_3 = b - a = \text{Milliequiv. of NaHCO}_3$$

Knowing the milliequivalents of the base and volume of the solution titrated, the normality (strength) of the bases can be calculated.

Solved Example 2-46

Both Na_2CO_3 and $NaHCO_3$ are present in an aqueous solution. In the presence of phenolphthalein indicator, 10 mL of this solution requires 2.5 mL of 0.1 M H_2SO_4 for titration. After this, methyl orange is added in the same solution and titration requires 5 mL M H_2SO_4. Calculate the concentration of Na_2CO_3 and $NaHCO_3$ in g L^{-1}.

Solution

Milliequiv. (a) of H_2SO_4 used in the presence of phenolphthalein indicator = $N \times V$ (mL) = $0.1 \times 2 \times 2.5 = 0.5$. Therefore,

$$a = 0.5 = \frac{1}{2} \text{ milliequiv. of Na}_2\text{CO}_3 \tag{1}$$

$$\text{Milliequiv. } (b) \text{ of NaHCO}_3 + \frac{1}{2} \times \text{Milliequiv. of Na}_2\text{CO}_3 \tag{2}$$

For Na_2CO_3 solution: From Eq. (1), we have

Milliequiv. of acid used by $Na_2CO_3 = 2 \times 0.5 = 1$. Suppose normality of Na_2CO_3 solution = N_1 and given that volume of Na_2CO_3 solution taken, V_1 = 10 mL, then

$$\text{Milliequiv. of Na}_2\text{CO}_3 \text{ taken} = N_1 \times V_1(\text{mL}) = 10\ N_1$$

Putting the milliequiv. of H_2SO_4 and Na_2CO_3 equal, we have $1 = 10\ N_1 \Rightarrow N_1 = 0.1$ N.
Now, strength (S) in g $L^{-1} = N_1 \times$ Equivalent weight $= 0.1 \times 53 = 53$ g L^{-1}.

For $NaHCO_3$ Solution: From Eqs. (1) and (2), milliequiv. of acid used by $NaHCO_3 = b - a = 1.0 - 0.5 = 0.5$.

Suppose normality of $NaHCO_3$ solution = N_2 and given that volume of $NaHCO_3$ solution taken, $V_2 = 10$ mL, then milliequiv. of $NaHCO_3$ taken = 10 N.
Now, putting the milliequiv. of H_2SO_4 and $NaHCO_3$ equal, we get $0.5 = 10\ N_2 \Rightarrow N_2 = 0.05$ N.
Now, strength (S) in g $L^{-1} = N_1 \times$ Equivalent weight $= 0.05 \times 84 = 4.2$ g L^{-1}.

Back Titration

Let us consider that we have an impure solid substance Z weighting W g and we are required to calculate the percentage purity of Z in the sample. We are also provided with two solutions X and Y, where the concentration of Y is known (N_1) and that of X is unknown. For the back titration to work, following conditions are to be satisfied.

1. Compounds X, Y and Z should be such that X and Y react with each other.
2. Compounds X and pure Z also react with each other, but the impurity present in Z does not react with X.

The reactions involved are

$$\begin{gathered} Z + X(\text{excess}) \rightarrow \text{Product1} \\ \text{Remaining } (X) + Y \rightarrow \text{Product2} \end{gathered} \tag{2.6}$$

Note: Product 1 should not react with Y
Now, milliequiv. of $Y = N_2\ V_2$ where N_2 and V_2 (mL) is the normality and volume of Y.
Initial milliequiv. of $X = N_1V_1$ where N_1 and V_1 (mL) is the normality and volume of X.
Remaining milliequiv. of X after reacting with $Y = N_1\ V_1 - N_2\ V_2$
Remaining milliequiv. of X = milliequiv. of Z, or

$$N_1V_1 - N_2V_2 = \frac{a \times 1000}{\text{Equivalent weight}}$$

where a is the weight of pure Z which is reacted, and is given by

$$a = \frac{\text{Molecular weight}(N_1V_1 - N_2V_2)}{n\text{-factor}}$$

n-Factor is an integer that relates stoichiometric quantities. In the above expression, n-factor is the ratio of molecular weight to equivalent weight.
Hence, the percentage purity of $Z = \dfrac{(N_1V_1 - N_2V_2)}{n\text{-factor}} \times \dfrac{\text{Molar mass of } Z}{W} \times 100$

Solved Example 2-47

20 g of sample of $Ba(OH)_2$ is dissolved in 10 mL. of 0.5 N HCl solution. The excess of HCl was titrated with 0.2 N NaOH. The volume of NaOH used was 10 cm^3. Calculate the percentage of $Ba(OH)_2$ in the sample.

Solution

Milliequiv. of HCl initially $= 10 \times 0.5 = 5$. Now,

Milliequiv. of NaOH consumed = Milliequiv. of HCl in excess $= 10 \times 0.2 = 2$

Therefore, milliequiv. of HCl consumed = milliequiv. of $Ba(OH)_2 = 5 - 2 = 3$.
Thus, equiv. of $Ba(OH)_2 = 3/1000 = 3 \times 10^{-3}$
Now, mass of $Ba(OH)_2$ = Equivalents × Equivalent weight $= 3 \times 10^{-3} \times (171/2) = 0.2565$ g.

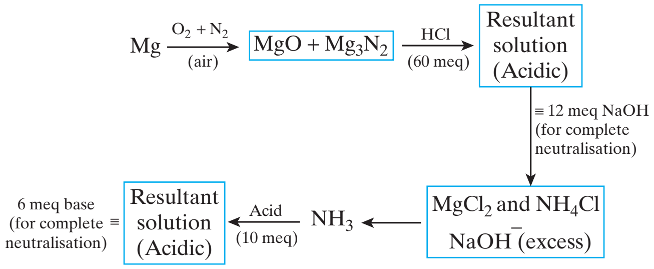
Therefore, $\%Ba(OH)_2 = \dfrac{0.2565}{20} \times 100 = 1.28\%$

Solved Example 2-48

A sample of Mg was burnt in air to give a mixture of MgO and Mg_3N_2. The ash was dissolved in 60 milliequiv. of KCl and the resulting solution was back titrated with NaOH. 12 milliequiv. of NaOH were required to reach the end point. An excess of NaOH was then added and the solution was distilled. The ammonia released was the trapped in 10 milliequiv. of second acid solution. Back titration of this solution required 6 milliequiv. of the base. Calculate the percentage of magnesium burnt to the nitride.

Solution

The reaction sequence can be summarized as shown:


Mg
$O_2 + N_2$
(air)
$MgO + Mg_3N_2$
HCl
(60 meq)
Resultant solution (Acidic)
≡ 12 meq NaOH (for complete neutralisation)
$MgCl_2$ and NH_4Cl
NaOH (excess)
NH_3
Acid
(10 meq)
Resultant solution (Acidic)
6 meq base (for complete neutralisation) ≡

The total milliequiv. of HCl = 60 and

Excess milliequiv. of HCl ≡ milliequiv. of NaOH used = 12

Milliequiv. of HCl used for ($MgO + Mg_3N_2$) = 60 – 12 = 48

Millimoles of HCl used = 48

$$MgO + 2HCl \rightarrow MgCl_2 + H_2O$$

$$Mg_3N_2 + HCl \rightarrow 3MgCl_2 + 2NH_4Cl$$

On adding NaOH, we get

$$NH_4Cl + NaOH \rightarrow NaCl + NH_3 + H_2O$$

Note: $MgCl_2$ is a salt of strong acid and strong base, so it is neutral.

$$\text{Milliequiv. of } NH_4Cl \equiv \text{Milliequiv. of NaOH used for } NH_4Cl = \text{Milliequiv. of } NH_3$$

Milliequiv. of NH_3 ≡ total milliequiv. of acid – Excess milliequiv. of acid used against base = 10 – 6 = 4

Now, milliequiv. of NH_3 = millimoles of NH_3.
But millimoles of NH_3 = 4 as valence factor = 1 for NH_3.

Thus, millimoles of $Mg_3N_2 = \frac{1}{2} \times$ millimoles of $NH_4Cl = \frac{1}{2} \times 4 = 2$

and millimoles of HCl consumed for $Mg_3N_2 = 2 \times 8 = 16$.
Thus, millimoles of HCl used for Mg = 48 – 16 = 32 ⇒ millimoles of MgO = millimoles of HCl = 16.
Now, we have the reactions

$$Mg + \tfrac{1}{2}O_2 \rightarrow MgO$$

and

$$3Mg + N_2 \rightarrow Mg_3N_2$$

From the reactions, we have millimoles of Mg burnt to form MgO = millimoles of MgO = 16.
Now, millimoles of Mg burnt to form Mg_3N_2 = 3 × millimoles of $Mg_3N_2 = 3 \times 2 = 6$.

Therefore,
$$\%\text{Mg burnt to form } Mg_3N_2 = \frac{6}{6+16} \times 100 = 27.27\%$$

2.9 | APPLICATIONS OF REDOX REACTIONS

Volume Strength of H_2O_2 Solution

The concentration of H_2O_2 is usually represented in terms of volume. If a sample of H_2O_2 is labeled as *x* volume, it means that 1 volume of H_2O_2 solution gives *x* volumes of O_2 gas at STP on complete decomposition. Consider the decomposition of H_2O_2 as

$$\underset{2\times 34\text{ g}}{2H_2O_2} \xrightarrow{\Delta} 2H_2O + \underset{22.\ 4\text{ L at STP}}{O_2}$$

As 22400 mL of O_2 gas is liberated by 68 g of H_2O_2 solution, therefore

$$x\text{ mL of } O_2 \text{ gas will be liberated by } \frac{68x}{22400} = \frac{17x}{5600}\text{ g of } H_2O_2 \text{ of } H_2O_2$$

It means that $\frac{17x}{5600}$ g of H_2O_2 will be present in 1 mL of solution. Hence,

1000 mL of solution contains $H_2O_2 = \frac{17x}{5600}\times 1000 = \frac{17x}{5.6}$

Now, strength (g L^{-1}) = normality × equivalent weight

or $$\frac{17x}{5.6} = N \times \frac{34}{2} \Rightarrow \text{strength}(x) = 5.6 \times N$$

Note:

For hydrogen peroxide remember the following relations:

1. Strength of H_2O_2 in % $= \frac{17}{56} \times$ Volume strength
2. Volume strength of $H_2O_2 = \frac{56}{17} \times$ Percentage
3. Volume strength of $H_2O_2 = 11.2 \times$ Molarity
4. Volume strength of $H_2O_2 = 5.6 \times$ Normality
5. Normality of $H_2O_2 = \frac{\text{Volume strength}}{5.6}$
6. Molarity of $H_2O_2 = \frac{\text{Volume strength}}{11.2}$
7. Strength of H_2O_2 in $\text{g L}^{-1} = \frac{\text{Volume strength} \times 68}{22.4}$

   or

   $\frac{\text{Volume strength} \times 34}{11.2}$
8. Strength of H_2O_2in g L^{-1} = Normality × Equivalent weight

   or

   Molarity × Molecular mass

Solved Example 2-49

A sample of H_2O_2 is x% by mass. If x mL of $KMnO_4$ are required to oxidize 1 g of this H_2O_2 sample, calculate the normality of $KMnO_4$ solution.

Solution

Suppose, mass of H_2O_2 solution = 100 g, mass of H_2O_2 present = x g.
Given that mass of H_2O_2 solution taken = 1 g. So,

Mass of H_2O_2 present in 1 g solution $= \frac{x}{100}$

Now,

$$\text{Equiv. of } H_2O_2 = \frac{\text{Weight}}{\text{Equivalent weight}} = \frac{x}{100 \times (34/2)}$$

Now, equiv. of $KMnO_4 = N \times V\text{ (L)} = N \times x \times 10^{-3}$. Putting equivalents of H_2O_2 and $KMnO_4$ equal, we get

$$\frac{x}{100 \times 17} = N \times x \times 10^{-3}$$

or normality of $H_2SO_4\,(N) = 0.59$ N

Solved Example 2-50

50 mL solution of H_2O_2 was treated with excess KI(s) and the solution was acidified with acetic acid. The liberated iodine required 40 mL 0.5 M $Na_2S_2O_3$ solution for the end point using starch as indicator. Find the molarity and volume strength of the H_2O_2 solution.

Solution

Milliequiv. of H_2O_2 in 50 mL = Milliequiv. of hypo = 40 × 0.5 = 20 milliequiv.
Now, normality = 20/50 = 0.4 N and molarity = normality/valence factor = 0.4/2 = 0.2 M
Thus, volume strength = $M \times 11.2 = 0.2 \times 11.2 = 2.24$ g L^{-1}

Solved Example 2-51

(a) Concentrated acid H_2SO_4 has a density of 1.8 g mL^{-1} and contains 49% acid by weight. Compute molarity of the solution. Also calculate the number of gram milliequiv. of H_2SO_4 contained in 1 L solution.

(b) What is the normality of a solution which is prepared by dissolving 100 mL of conc. H_2SO_4 in part **(a)** in sufficient water to make 500 mL of solution?

(c) If we take 50 mL sample of above solution [in part **(b)**], find number of millimoles and milliequivalents in the sample.

Solution

(a) Using the expression

$$\text{Molarity} = \frac{10 \times \%\text{Weight} \times \text{Density}}{M_B}$$

Substituting given values %weight = 49, density = 1.8 g mL^{-1} and molecular weight = 98, we have

$$\text{Molarity}(M) = \frac{10 \times 49 \times 1.8}{98} = 9.0 \text{ M}$$

To calculate gram milliequiv., it is better to calculate normality first.

$$N = \text{Valence factor} \times M = 2 \times 9 = 18 \text{ N}$$

where the valence factor = basicity of the acid = 2 for H_2SO_4.
Therefore, gram milliequiv. = $N \times V_1 = 1 \times 18 = 18$ gram milliequiv. are contained in 1 L of given solution.

(b) From part **(a)**, we have N of H_2SO_4 = 18. Then gram milliequiv. in 100 cm^3 of conc. H_2SO_4 is

$$\frac{18.0 \times 100}{1000} = 1.8$$

So, 1.8 gram milliequiv. of concentrated acid are to be added in water to make 500 mL solution

Normality of required solution (N) = $\frac{\text{gram milliequiv.}}{V(\text{L})} = \frac{1.8}{500/1000} = 3.6 \text{ N}$ $\frac{1.8}{500/1000} = 3.6$

(c) Milliequivalents = Normality × Volume (in mL) = $N \times V_1 = 3.6 \times 50 = 180$ milliequiv.

Millimoles = Molarity × Volume (in mL) = $M \times V_1 = \frac{3.6}{2} \times 50 = 90$ millimoles
where molarity = normality/2 as H_2SO_4 is a dibasic acid.

Percentage Labeling of Oleum

Oleum (fuming H_2SO_4) acid contains SO_3 dissolved in H_2SO_4. When water is added to oleum, SO_3 reacts to form H_2SO_4, thus the mass of the solution increases.

$$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$$

The % labeling of oleum is equal to total mass of H_2SO_4 present in in oleum after diluting 100 g of sample with desired amount of water or

%Labeling of oleum = Mass of H_2SO_4 initially present + Mass of H_2SO_4 produced on dilution

Solved Example 2-52

Calculate the composition of 109% oleum.

Solution

Let the mass of SO_3 in the sample be w g, then the mass of H_2SO_4 would be $(100 – w)$ g. On dilution, the reaction is

$$\underset{80\text{ g}}{SO_3} + \underset{18\text{ g}}{H_2O} \rightarrow H_2SO_4$$

Moles of SO_3 in oleum $= \dfrac{w}{80} =$ Moles of H_2SO_4 formed after dilution.

Therefore, mass of H_2SO_4 formed on dilution $= \dfrac{98w}{80}$

Total mass of H_2SO_4 present in oleum after dilution $= \dfrac{98w}{80} + (100 - w) = 109$ g

Solving, we find that the oleum sample contains 40% SO_3 and 60% H_2SO_4.

Solved Example 2-53

A sample of fuming sulphuric acid (oleum) contains H_2SO_4, SO_3, SO_2. For analysis, 2.0 g of sample was dissolved in water to make a 500 mL solution. For 50 mL of this solution on titration (in presence of methyl orange), 45.0 mL of 0.1 N NaOH was used up. On other hand, for 100 mL of the same solution, 2.0 mL of 0 1 N of iodine was consumed where I_2 is reduced to I^- ions, Determine the percentage composition of oleum sample. [Note that in presence of methyl orange, H_2SO_3 is only half neutralized.]

Solution

Let the mass of $H_2SO_4 = x$ g, mass of $SO_3 = y$ g and mass of $SO_2 = z$ g. So, we have

$$x + y + z = 20 \quad (1)$$

In 50 mL sample, we have

$$SO_2 + H_2O \rightarrow H_2SO_3 \xrightarrow[\text{(Methyl orange)}]{\text{NaOH}} HSO_3^-$$

Thus, from the reaction, we have

Gram milliequiv. of NaOH ≡ Gram milliequiv. of H_2SO_4
+Gram milliequiv. of SO_3
+1/2 Gram milliequiv.of SO_2

Substituting values, we get

$$0.1 \times \frac{45}{1000} = \left(\frac{x}{10}\right) \times \frac{1}{98/2} + \left(\frac{y}{10}\right) \times \frac{1}{80/2} + \frac{1}{2} \times \left(\frac{z}{10}\right) \times \frac{1}{64/1} \quad (2)$$

In 100 mL sample, only SO_2 reacts with I_2

$$I_2 + \overset{+4}{SO_2} \rightarrow I^- + \overset{+6}{SO_4^{2-}}$$

So, gram milliequiv. of I_2 ≡ gram milliequiv. of SO_2

or
$$0.1 \times \frac{2}{1000} = \left(\frac{z}{5}\right) \times \frac{1}{64/2} \quad (3)$$

Solving Eqs. (3), we get $z = 0.032$ g. Now, substituting value of z in Eqs. (1) and (2), and solving, we get $x = 1.028$ g and $y = 0.94$ g.
Hence, the percentage composition is as follows:

$$\%H_2SO_4 = \frac{1.028}{2} \times 100 = 51.4\%$$

$$\%SO_3 = \frac{0.94}{2} \times 100 = 47\%$$

$$\%SO_2 = \frac{0.032}{2} \times 100 = 1.6\%$$

Other Applications

Redox reactions form the basis of many important chemical reactions with applications in diverse fields. Some important applications are listed as follows.

1. **In industrial manufacture of chemicals:** Many compounds such as chlorine gas, sodium hydroxide, potassium hydroxide are produced on industrial scale by electrolysis that is based on redox reaction.
2. **In metallurgy:** Metal oxides obtained by metallurgical processes are reduced to metals by suitable reducing agents through redox reactions. The reduction may be carried out in electrolytic cell as in case of Al_2O_3 or in blast furnace as in case of Fe_2O_3.

   Metal displacement reactions also find wide application in metallurgical process to obtain pure metals from their ores. In general, a metal can displace and reduce the ions of any of the metals which are below that metal in the reactivity series. This property is used in the thermite reaction for preparing small quantities of metallic iron, wherein aluminium reduces iron(III) oxide to iron, thus becoming aluminium oxide in the process:

$$2Al(s) + Fe_2O_3(s) \rightarrow 2Fe(s) + Al_2O_3(s)$$

The Kroll process for preparing titanium is also based on the same property, wherein magnesium is used to extract titanium from titanium tetrachloride, forming magnesium chloride in the process:

$$2\,Mg(s) + TiCl_4(l) \rightarrow Ti(s) + 2MgCl_2(s)$$

3. **In photosynthesis:** The photosynthesis reaction that converts carbon dioxide and water in green plants in the presence of chlorophyll and sunlight to glucose and oxygen is a redox reaction. Carbon dioxide is reduced to carbohydrate and water is oxidized to oxygen.

$$6CO_2(g) + 6H_2O(l) \xrightarrow[\text{Sunlight}]{\text{Chlorophyll}} C_6H_{12}O_6(aq) + 6O_2(g)$$

4. **In combustion of fuels:** Fuels such as natural gas, petrol, kerosene, etc. are examples of hydrocarbons, that is, they contain hydrogen and carbon. When they are burnt in excess of air/oxygen, the products of combustion are carbon dioxide and water along with release of large amount of energy.

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

This is also an example of a redox reaction in which hydrocarbon is oxidized to CO_2 and oxygen is reduced to water. The oxidation of glucose in the living cells also proceeds similarly through a redox reaction.

$$C_6H_{12}O_6(aq) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$$

5. **In batteries and electrochemical cells:** The electrode processes in batteries or electrochemical cells take place through redox reactions, between metal electrodes and metal salts as electrolytes.
6. **In quantitative estimations:** Redox reactions form the basis of the titrations carried out for quantitative analysis of different species in solution.

Solved Example 2-54

In the standardization of $Na_2S_2O_3$ using $K_2Cr_2O_7$ by iodometry, the equivalent mass of $K_2Cr_2O_7$ is **(IIT-JEE 2001)**

(A) (molar mass)/2

(B) (molar mass)/6

(C) (molar mass)/3

(D) same as molar mass

Solution

(B) As this is a redox titration involving gain of electrons, equivalent mass = (molar mass)/number of electrons involved = (molar mass)/6. The reaction is

$$Cr_2O_7^{2-} + 14\,H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

Solved Example 2-55

All the iron in a 2.0 g sample of an iron ore was dissolved in an acidic solution and converted to Fe^{2+}, which was then titrated with 0.1000 M $KMnO_4$ solution. In the titration, the iron was oxidized to Fe^{3+}. The titration required 27.45 mL of the $KMnO_4$ solution to reach the end point.

(a) How many grams of iron were in the sample?

(b) What was the percentage of iron in the sample?

(c) If the iron was present in the sample as Fe_2O_3, what was the percentage by mass of Fe_2O_3 in the sample?

Solution

(a) The skeleton equation for the reaction is

$$Fe^{2+} + MnO_4^- \rightarrow Fe^{3+} + Mn^{2+}$$

Balancing it by the ion–electron method for acidic solutions gives

$$5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$$

The number of moles of $KMnO_4$ consumed in the reaction is calculated from the volume of the solution used in the titration and its concentration.

$$0.02745\text{ L }KMnO_4 \times \frac{0.1000\text{ mol }KMnO_4}{1.000\text{ L }KMnO_4}$$
$$= 0.002745\text{ mol }KMnO_4$$

Next, we use the coefficients of the equation to calculate the number of moles of Fe^{2+} that reacted. The chemical equation tells us five moles of Fe^{2+} react per mole of MnO_4^- consumed.

$$0.02745\text{ mol }KMnO_4 \times \frac{5\text{ mol }Fe^{2+}}{1\text{ mol }KMnO_4}$$
$$= 0.01372\text{ mol }Fe^{2+}$$

This is the number of moles of iron in the ore sample, so the mass of iron in the sample is

$$0.01372\text{ mol Fe} \times \frac{55.845\text{ g Fe}}{1\text{ mol Fe}} = 0.7662\text{ g Fe}$$

(b) Next we calculate the percentage of iron in the sample, which is the mass of iron divided by the mass of the sample, all multiplied by 100%.

$$\%\text{Fe} = \frac{\text{Mass of Fe}}{\text{Mass of the sample}} \times 100\%$$

Substituting gives

$$\%\text{Fe} = \frac{0.7662\text{ g Fe}}{2.0\text{ g sample}} \times 100\% = 38.31\%\text{ Fe}$$

(c) The chemical formula for the iron oxide gives us that

$$1\text{ mol }Fe_2O_3 = 2\text{ mol Fe}$$

This provides the conversion factor for determining how many moles of Fe_2O_3 were present in the sample. Working with the number of moles of Fe, we get

$$0.01372\text{ mol Fe} \times \frac{1\text{ mol }Fe_2O_3}{2\text{ mol Fe}} = 0.006860\text{ mol }Fe_2O_3$$

This is the number of moles of Fe_2O_3 in the sample. The formula mass of Fe_2O_3 is 159.69 g mol^{-1}, so the mass of Fe_2O_3 in the sample was

$$0.006860\text{ mol }Fe_2O_3 \times \frac{159.69\text{ g }Fe_2O_3}{1\text{ mol }Fe_2O_3}$$
$$= 1.095\text{ g }Fe_2O_3$$

Finally, the percentage of Fe_2O_3 in the sample was

$$\%Fe_2O_3 = \frac{1.095\text{ g }Fe_2O_3}{2.0\text{ g sample}} \times 100\% = 54.75\%\ Fe_2O_3$$

Thus, the sample contained 54.75% Fe_2O_3.

Solved Example 2-56

A 15.00 mL sample of a solution containing oxalic acid, $H_2C_2O_4$, was titrated with 0.02 M $KMnO_4$. The titration required 18.30 mL of the $KMnO_4$ solution. What was the molarity of the $H_2C_2O_4$ solution? In the reaction, oxalate ion ($C_2O_4^{2-}$) is oxidized to CO_2 and MnO_4^- is reduced to Mn^{2+}.

Solution

First we need a balanced equation:

$$C_2O_4^{2-} \rightarrow CO_2 \rightarrow CO_2$$
$$MnO_4^- \rightarrow Mn^{2+} \rightarrow Mn^{2+}$$

Balance the atoms

$$C_2O_4^{2-} \rightarrow CO_2 \rightarrow 2CO_2$$
$$8H^+ + MnO_4^- \rightarrow Mn^{2+} + 4H_2O$$

Balance the charges

$$C_2O_4^{2-} \rightarrow CO_2 + 2e^-$$
$$5e^- + 8H^+ + MnO_4^- \rightarrow Mn^{2+} + 4H_2O$$

Add the reactions together

$$5C_2O_4^{2-} + 16H^+ + 2MnO_4^- \rightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$$

$$\text{Moles of }C_2O_4^{2-} = 18.30 \times \frac{1}{1000} \times \frac{0.02000}{1} \times \frac{5}{2}$$
$$= 0.0009150\text{ mol of }C_2O_4^{2-}$$

$$[H_2C_2O_4] = \frac{0.0009150}{15.00} \times \frac{1000}{1} \times \frac{1}{1} = 0.06100\text{ M}$$

Solved Example 2-57

A sample of a tin ore weighing 0.3 g was dissolved in an acid solution and all the tin in the sample was changed to tin(II). In a titration, 8.08 mL of 0.05 M $KMnO_4$ solution was required to oxidize the tin(II) to tin(IV).

(a) What is the balanced equation for the reaction in the titration?

(b) How many grams of tin were in the sample?

(c) What was the percentage by mass of tin in the sample?

(d) If the tin in the sample had been present in the compound SnO_2, what would have been the percentage by mass of SnO_2 in the sample?

Solution

(a) $(Sn^{2+} \rightarrow Sn^{4+} + 2e^-) \times 5$

$$(MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O) \times 2$$

$$5Sn^{2+} + 2MnO_4^- + 16H^+ \rightarrow 5Sn^{4+} + 2Mn^{2+} + 8H_2O$$

(b) $Sn = 8.08 \times \frac{0.0500}{1000} \times \frac{1}{1} \times \frac{5}{2} \times \frac{1}{1} \times \frac{118.71}{1} = 0.120\,g$

(c) $\% \ Sn = \frac{0.120}{0.300} \times 100 = 40.0\% \ Sn$

(d) $SnO_2 = 8.08 \times \frac{0.0500}{1000} \times \frac{1}{1} \times \frac{5}{2} \times \frac{1}{1} \times \frac{150.71}{1} = 0.152\,g$

$$\% \ SnO_2 = \frac{0.152}{0.300} \times 100 = 50.7\% \ SnO_2$$

Solved Example 2-58

A solution of 0.2 g of a compound containing cupric and oxalate ions on titration with 0.02 M potassium permanganate in presence of sulphuric acid consumes 22.6 mL of the oxidant. The resultant solution is neutralized with sodium carbonate, acidified with dilute acetic acid and treated with excess of KI. The iodine liberated required 11.3 mL of 0.05 M sodium thiosulphate solution for complete reduction. Find the mole ratio of two ions. Also write down the balanced redox reaction involved in the above titrations.

Solution

Cu^{2+} ion cannot be oxidized, so only $C_2O_4^{2-}$ will be oxidized by $KMnO_4$.

$$5C_2O_4 + 2Mn + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

2 millimoles of $MnO_4^- \equiv 5$ millimoles of $C_2O_4^{2-}$ ions $= 0.02 \times 22.6$ millimoles of oxalate ions

From the following reactions, we have

$$Cu^{2+} + KI \rightarrow Cu^+ (\text{not } Cu^0)$$

$$2Cu^{2+} + 2I^- \rightarrow I_2 + 2Cu^+$$

$$I_2 + S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

2 millimoles of $S_2O_3^{2-} \equiv 1$ millimole of I_2

or (0.05×11.3) millimole $S_2O_3^{2-} \equiv 1/2\ (0.05 \times 11.3)$ millimoles of $I_2 = 0.2825$ millimoles of I_2

Also, 1 millimoles of $I_2 \equiv 2$ millimoles of Cu^{2+}

0.2825 millimoles of $I_2 \equiv 2 \times 0.2825$ millimoles of $Cu^{2+} =$ 0.565 millimoles of Cu^{2+}

So, the mole ratio of $\frac{C_2O_4^{2-}}{Cu^{2+}} = \frac{1.13}{0.565} = 2$

Solved Example 2-59

Find the amount of iron pyrites (FeS_2) which is sufficient to produce enough SO_2 on roasting (hearing in excess of O_2) such that it (SO_2) completely decolorize a solution of $KMnO_4$ containing 15.8 g L^{-1} of it.

The equation are as follows:

$$FeS_2 + O_2 \rightarrow Fe_2O_3 + SO_2$$

and $$KMnO_4 + SO_2 \rightarrow H_2SO_4 + KHSO_4$$

Solution

First, calculation the amount of SO_2 required to decolorize 15.8 g L^{-1} of $KMnO_4$ solution. For this, we need to balance the following chemical reaction.

$$KMnO_4 + SO_2 \rightarrow H_2SO_4 + KHSO_4$$

Writing the half reactions involving ions, we get

$$K\overset{+7}{Mn}O_4 + \underbrace{\overset{+4}{S}O_2 \rightarrow KH\overset{+6}{S}O_4}_{2e^-\ \text{oxidation}} + H_2\overset{+6}{S}O_4$$

There is decrease in oxidation state in S from +4 to +6, so there is decrease in oxidation state of Mn from +7 to +2. The half reactions are

$$(\overset{+4}{S}O_2 \rightarrow \overset{+6}{S}O_4^{2-} + H\overset{+6}{S}O_4^- + 2e^-)\times 5$$

$$(\overset{+7}{Mn} + 5e^- \rightarrow Mn^{2+})\times 2$$

Adding the two equations, we get

$$2\overset{+7}{Mn} + 5\overset{+4}{S}O_2 \rightarrow 5SO_4^{2-} + 5H\overset{+6}{S}O_4^- + 2Mn^{2+}$$

To balance the number of S atoms, we can write $2Mn^{2+} + 2SO_4^{2-}$ as $2MnSO_4$. Now, comparing with the unbalanced molecular equation and balancing the number of S atoms, we have

$$2KMnO_4 + 5SO_2 \rightarrow H_2SO_4 + 2KHSO_4 + 2MnSO_4$$

Now, to balance the number of H and O atoms, we add $2H_2O$ on the left to get the balanced equation as

$$2KMnO_4 + 5SO_2 + 2H_2O \rightarrow H_2SO_4 + 2KHSO_4 + 2MnSO_4$$

Now, from the stoichiometry of balanced equation, we have:

$$2 \text{ mol of } KMnO_4 \equiv 5 \text{ mol of } SO_2$$

The number of moles in 15.8 g L^{-1} of $KMnO_4$ is:

$$\frac{\text{Given weight}}{\text{Molecular weight}} = \frac{15.8}{158} = 0.1 \text{ mol}$$

This means 1.0 L of $KMnO_4$ contains 0.1 mol

Hence, moles of SO_2 required $= \frac{5}{2}(0.1) = 0.25$ mol

Now, to calculate the amount of pyrites, we have to balance the reaction

$$FeS_2 + O_2 \rightarrow Fe_2O_3 + SO_2$$

Now, writing oxidation states, we get

$$\underbrace{\overset{+2}{Fe}S_2 + O_2 \rightarrow \overset{+3}{Fe}_2O_3}_{2\times e^- = 2e^-\ (\text{oxidation})} + \overset{+4}{S}O_2$$

Balancing the number of S and O atoms, we get

$$4FeS_2 + 12O_2 \rightarrow 2Fe_2O_3 + 8SO_2$$

8 mol of $SO_2 \equiv 4$ moles of FeS_2

0.25 mol of $SO_2 \equiv \frac{4}{8} \times (0.25)$ mol of $FeS_2 = 0.125$ mol of FeS_2

Therefore, mass of $FeS_2 = 0.125 \times (2 \times 32 + 56 = 120) = 15$ g.

SOLVED OBJECTIVE QUESTIONS FROM PREVIOUS YEAR PAPERS

1. When I^- is oxidized by MnO_4^- in alkaline medium, I^- converts into **(IIT-JEE 2004)**

(A) IO_3^- (B) I_2
(C) IO_4^- (D) IO^-

Solution

(A) The reactions involved are

$$\begin{array}{l} 2KMnO_4 + 2KOH \rightarrow 2K_2MnO_4 + H_2O + O \\ 2K_2MnO_4 + 2H_2O \rightarrow 2MnO_2 + 4KOH + 2O \\ \hline 2KMnO_4 + H_2O \rightarrow 2MnO_2 + 2KOH + 3[O] \\ KI + [O] \rightarrow KIO_3 \\ \hline 2KMnO_4 + KI + H_2O \rightarrow 2KOH + 2MnO_2 + KIO_3 \end{array}$$

2. Which of the following is not oxidized by O_3? **(IIT-JEE 2005)**

(A) KI (B) $KMnO_4$
(C) K_2MnO_4 (D) $FeSO_4$

Solution

(B) $KMnO_4$ is not oxidized by O_3 because Mn in $KMnO_4$ is in its maximum possible oxidation state (i.e. +6). It cannot increase its oxidation state beyond that.

3. Match the extraction processes with metals **(IIT-JEE 2006)**

Column I	Column II
(A) Self reduction	(p) Lead
(B) Carbon reduction	(q) Silver
(C) Complex formation and displacement by metal	(r) Copper
(D) Decomposition of iodide	(s) Boron

Solution

A → (p, r); B → (p, r); C → (q); D → (s)

(A) Self reduction: $PbS + 2PbO \rightarrow 3Pb + SO_2$ and $Cu_2S + 2Cu_2O \rightarrow 6Cu + SO_2$

(B) Carbon reduction: $PbO + C \rightarrow Pb + CO$ and $2CuO + C \rightarrow 2Cu + CO$

(C) Complex formation and displacement by metal: $Ag_2S + 4NaCN \rightarrow 2Na[Ag(CN)_2] + Na_2S$ and $2Na[Ag(CN)_2] + Zn \rightarrow 2Ag + Na_2[Zn(CN)_4]$

(D) Decomposition of iodide:
BI_3 (heated under red hot tungsten) $\rightarrow B + 3I$ (iodide)

4. Consider a titration of potassium dichromate solution with acidified Mohr's salt solution using diphenylamine as indicator. The number of moles of Mohr's salt required per mole of dichromate is **(IIT-JEE 2007)**

(A) 3
(B) 4
(C) 5
(D) 6

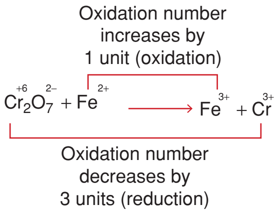
Solution

(D) The skeletal ionic equation is

$$Cr_2O_7 + Fe^{2+} \rightarrow Fe^{3+} + Cr^{3+}$$

First, calculate the oxidation number of Cr

$$2x + 7(-2) = -2 \Rightarrow 2x - 14 = -2 \Rightarrow x = +6$$


Oxidation number increases by 1 unit (oxidation)
+6
2–
2+
Cr2O7 + Fe
Fe 3+ + Cr 3+
Oxidation number decreases by 3 units (reduction)

In Cr_2O_7, the decrease in oxidation number is by 3 units per atom and since 2 atoms of chromium are involved so the total decrease is $3 \times 2 = 6$.

$$Cr_2O_7 + 6e^- \rightarrow Cr^{3+}$$

$$(Fe^{2+} \rightarrow Fe^{3+} + e^-) \times 6$$

We need to multiply this equation by 6. So the n factor for $Cr_2O_7 = 6$ and for $Fe^{2+} = 1$. Thus, to reduce 1 mol of dichromate, 6 mol of Fe^{2+} is required.

5. Match the reaction with the type of reaction/nature of product

Column I	Column II
(A) $O_2^- \rightarrow O_2 + O_2^{2-}$	(p) Redox reaction
(B) $CrO_4^{2-} + H^+ \rightarrow$	(q) One of the products has trigonal planar structure.
(C) $MnO_4^- + NO_2^- + H^+ \rightarrow$	(r) Dimeric bridged tetrahedral metal ion.
(D) $NO_3^- + H_2SO_4 + Fe^{2+} \rightarrow$	(s) Disproportionation

(IIT-JEE 2007)

Solution

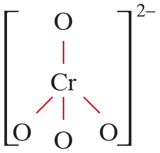
A → (p, s); B → (r); C → (p, q); D → (p)

(A) Consider the reaction $O_2^- \rightarrow O_2 + O_2^{2-}$

This is a redox reaction and to be more specific this is a disproportion reaction because in this case, both the oxidation number of oxygen (from –1 to 0 and –2) is increasing as well as decreasing at the same time.

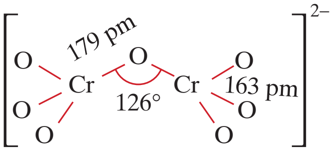
(B) The chromate ion has tetrahedral structure in which four atoms are around chromium atom and are oriented in tetrahedral arrangement.

CrO_4^{2-}



The dichromate ion consists of two tetrahedral units sharing one corner with Cr–O–Cr bond angle of 126°.

$Cr_2O_7^{2-}$



(C) This reaction is also a redox reaction, since both reduction and oxidation are involved and also the product formed, that is, NO_3^- has a trigonal planar structure.

$$2MnO_4^- + 5NO_2^- + 6H^+ \rightarrow Mn^{2+} + 3H_2O + 5NO_3^-$$

(D) This reaction is also a redox reaction since both reduction and oxidation are involved.

6. The oxidation number of Mn in the product of alkaline oxidative fusion of MnO_2 is __________. **(IIT-JEE 2009)**

Solution

(6) $$2MnO_2 + 4KOH + O_2 \rightarrow \underset{\text{Potassium manganate}}{2K_2MnO_4} + 2H_2O$$

Let the oxidation number of Mn be x, then we have

$$2(+1) + x + 4(-2) = 0 \Rightarrow 2 + x - 8 = 0$$

$$x - 6 = 0 \Rightarrow x = +6$$

7. Among the following, the number of elements showing only one non-zero oxidation state is __________.
O, Cl, F, N, P, Sn, Tl, Na, Ti **(IIT-JEE 2010)**

Solution

(2) F and Na show only one non-zero oxidation state.

8. The value of n in the molecular formula $Be_nAl_2Si_6O_{18}$ is __________. **(IIT-JEE 2010)**

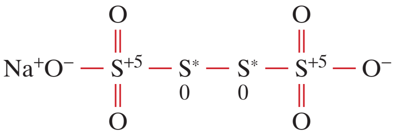
Solution

(3) According to the charge balance in a molecule, $2n + 2 \times (+3) + 6 \times (+4) + 18 \times (-2) = 0 \Rightarrow n = 3$. Thus, the formula becomes $Be_3Al_2Si_6O_{18}$ (beryl).

9. The difference in the oxidation number of the two types of sulphur atoms in $Na_2S_4O_6$ is __________. **(IIT-JEE 2011)**

Solution

(5) S* are in 0 oxidation state and S are in +5 oxidation state. Their difference is 5.



$$Na^+O^- - \overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S^{+5}}} - \underset{0}{S^*} - \underset{0}{S^*} - \overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S^{+5}}} - O^-$$

10. Reaction of Br_2 with Na_2CO_3 in aqueous solution gives sodium bromide and sodium bromate with evolution of CO_2 gas. The number of sodium bromide molecules involved in the balanced chemical equation is __________. **(IIT-JEE 2011)**

Solution

(5) The balanced chemical equation is:

$$3Na_2CO_3 + 3Br_2 \rightarrow 5NaBr + NaBrO_3 + 3CO_2$$

11. The reaction of white phosphorus with aqueous NaOH gives phosphine along with another phosphorus containing compound. The reaction type; the oxidation states of phosphorus in phosphine and the other product are, respectively,

(A) redox reaction; –3 and –5
(B) redox reaction; +3 and +5
(C) disproportionation reaction; –3 and +1
(D) disproportionation reaction; –3 and +3

(IIT-JEE 2012)

Solution

(C) According to the reaction
$P_4 + NaOH + 3H_2O \rightarrow PH_3 + 3NaH_2PO_2$
Oxidation state of phosphorus in P_4 is zero while in PH_3 it is –3 and in NaH_2PO_2, it is +1. This shows that this is a type of disproportionation reaction because there is an increase as well as decrease in the oxidation state of phosphorus.

12. For the reaction

$$I^- + ClO_3^- + H_2SO_4 \rightarrow Cl^- + HSO_4^- + I_2$$

The correct statements(s) in the balanced equation is/are

(A) stoichiometric coefficient of HSO_4^- is 6.
(B) iodide is oxidized.
(C) sulphur is reduced.
(D) H_2O is one of the products.

(JEE Advanced 2014)

Solution

(A), (B), (D) The correct balanced equation is

$$6I^- + 6ClO_3^- + 6H_2SO_4 \rightarrow Cl^- + 6HSO_4^- + 3I_2 + 3H_2O$$

Since I^- is getting converted into I_2, hence it is getting oxidized. The stoichiometric coefficient of HSO_4^- is 6 and H_2O is one of the products.

13. Consider the following list of reagents:
Acidified $K_2Cr_2O_7$, alkaline $KMnO_4$, $CuSO_4$, H_2O_2, Cl_2, O_3, $FeCl_3$, HNO_3, and $Na_2S_2O_3$.
The total number of reagents that can oxidize aqueous iodide to iodine is _____. **(JEE Advanced 2014)**

Solution

(7) The reactions involved are
$K_2Cr_2O_7 + I^- + H^+ \rightarrow I_2$ $CuSO_4 + I^- \rightarrow I_2$
$H_2O_2 + I^- \rightarrow I_2$ $Cl_2 + I^- \rightarrow I_2$
$FeCl_3 + I^- \rightarrow I_2$ $HNO_3 + I^- \rightarrow I_2$
Apart from this ozone also oxidizes aqueous iodide to liberate iodine gas. So in all there are seven such reagents.

14. Hydrogen peroxide in its reaction with KIO_4 and NH_2OH respectively, is acting as a

(A) reducing agent, oxidizing agent
(B) reducing agent, reducing agent
(C) oxidizing agent, oxidizing agent
(D) oxidizing agent, reducing agent

(JEE Advanced 2014)

Solution

(A) The reactions involved are
$H_2O_2 + KIO_4 \rightarrow KIO_3 + H_2O + O_2$ (Reducing agent)
$H_2O_2 + NH_2OH \rightarrow H_2O + N_2O_3$ (Oxidizing agent)

15. Excess of KI reacts with $CuSO_4$ solution and then $Na_2S_2O_3$ solution is added to it. Which of the statements is incorrect for this reaction? **(AIEEE 2004)**

(A) Cu_2I_2 is reduced (B) Evolved I_2 is reduced
(C) $Na_2S_2O_3$ is oxidized (D) CuI_2 is formed

Solution

(D) CuI_2 is formed as

$$2CuSO_4 + \underset{\text{(excess)}}{4KI} \rightarrow 2K_2SO_4 + CuI_2 + I_2$$

16. Among the properties (I) reducing (II) oxidizing (III) complexing, the set of properties shown by CN^- ion towards metal species is **(AIEEE 2004)**

(A) I, II (B) I, II, III
(C) III, I (D) II, III

Solution

(C) It is oxidizing as N is in highest oxidation state of +5; and CN^- is complexing as it forms bidentate complexes with binding sites C and N.

17. To neutralize completely 20 mL of 0.1 M aqueous solution of phosphorous acid (H_3PO_3), the volume of 0.1 molal aqueous KOH solution required is **(AIEEE 2004)**

(A) 10 mL (B) 60 mL
(C) 40 mL (D) 20 mL

Solution

(C) Using the molarity equation, we get
$n_1 \times M_1 \times V_1 = n_2 \times M_2 \times V_2$,

$$2 \times 0.1 \times 20 = 1 \times 0.1 \times V_2 \Rightarrow V_2 = \frac{2 \times 0.1 \times 20}{0.1} = 40 \text{ mL}$$

18. Which of the following chemical reactions depicts the oxidizing behavior of H_2SO_4? **(AIEEE 2006)**

(A) $2HI + H_2SO_4 \rightarrow I_2$
(B) $Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 + 2H_2O$
(C) $NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$
(D) $2PCl_5 + H_2SO_4 \rightarrow 2POCl_3 + 2HCl + SO_2Cl_2$

Solution

(A) $2HI + H_2SO_4 \rightarrow I_2 + SO_2 + 2H_2O$

On left hand side, oxidation state of sulphur = 6
On right hand side, oxidation state of sulphur = 4
There is a decrease of oxidation state of sulphur from +6 in sulphuric acid to +4 in sulphur dioxide. It means that H_2SO_4 is reduced and iodide ions are oxidized to iodine by conc. H_2SO_4.

19. What products are expected from the disproportionation reaction of hypochlorous acid? **(AIEEE 2006)**

(A) $HClO_3$ and Cl_2O
(B) $HClO_2$ and $HClO_4$
(C) HCl and Cl_2O
(D) HCl and $HClO_3$

Solution

(D) Exchange of chlorine atoms of reactants occurs during the reaction.

$$2ClO_2 + HOCl + H_2O \rightarrow 3H^+ + 2ClO_3^- + 3Cl^-$$

20. Amount of oxalic acid present in a solution can be determined by its titration with $KMnO_4$ solution in the presence of H_2SO_4. The titration gives unsatisfactory result when carried out in the presence of HCl, because HCl

(A) gets oxidized by oxalic acid to chlorine.
(B) furnishes H^+ ions in addition to those from oxalic acid.
(C) reduces permanganate to Mn^{2+}.
(D) oxidizes oxalic acid to carbon dioxide and water.

(AIEEE 2008)

Solution

(C) MnO_4^- gets easily reduced to Mn^{2+} in the presence of HCl, hence is not used.

21. Experimentally it was found that a metal oxide has formula $M_{0.98}O$. Metal M, is present as M^{2+} and M^{3+} in its oxide. Fraction of the metal which exists as M^{3+} would be

(A) 4.08%
(B) 6.05%
(C) 5.08%
(D) 7.01%

(JEE Main 2013)

Solution

(A) Given, metal oxide = $M_{0.98}O$. If x ions of M are in +3 state, then $3x + (0.98 - x) \times 2 = 2 \Rightarrow x = 0.04$.
So, the percentage of metal in +3 state would be

$$\frac{0.04}{0.98} \times 100 = 4.08\%$$

22. Consider the following reaction

$$xMnO_4^- + yC_2O_4^{2-} + zH^+ \rightarrow xMn^{2+} + 2yCO_2 + \tfrac{z}{2}H_2O$$

The values of x, y and z in the reaction are, respectively

(A) 2, 5 and 8
(B) 2, 5 and 16
(C) 5, 2 and 8
(D) 5, 2 and 16

(JEE Main 2013)

Solution

(B) The balanced equation is

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

Hence, $x = 2, y = 5, z = 16$

23. In which of the following reactions H_2O_2 acts as a reducing agent?

(i) $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$
(ii) $H_2O_2 - 2e^- \rightarrow O_2 + 2H^+$
(iii) $H_2O_2 + 2e^- \rightarrow 2OH^-$
(iv) $H_2O_2 + 2OH^- - 2e^- \rightarrow O_2 + 2H_2O$

(A) (i), (ii)
(B) (iii), (iv)
(C) (i), (iii)
(D) (ii), (iv)

(JEE Main 2014)

Solution

(D) The oxidation states of the species are as follows:

(i) $H_2\overset{-1}{O}_2 + 2H^+ + 2e^- \rightarrow 2H_2\overset{-2}{O}$

(ii) $H_2\overset{-1}{O}_2 - 2e^- \rightarrow \overset{0}{O}_2 + 2H^+$

(iii) $H_2\overset{-1}{O}_2 + 2e^- \rightarrow 2\overset{-2}{O}H^-$

(iv) $H_2\overset{-1}{O}_2 + 2\overset{-2}{O}H^- - 2e^- \rightarrow \overset{0}{O}_2 + 2H_2\overset{-2}{O}$

In (ii) and (iv) H_2O_2 acts as a reducing agent as it loses electrons to reduces the other species and itself undergoes oxidation.

24. From the following statements regarding H_2O_2, choose the **incorrect** statement:

(A) It decomposes on exposure to light.
(B) It has to be stored in plastic or wax lined glass bottles in dark.
(C) It has to be kept away from dust.
(D) It can act only as an oxidizing agent.

(JEE Main 2015)

Solution

(D) The oxidation state of oxygen in H_2O_2 is –1 (peroxide). So, oxygen can increase and decrease its oxidation number which means it can act as a reducing as well as an oxidizing agent.

REVIEW QUESTIONS

1. Consider the following species: Cl_2, Cl^-, ClO^-, ClO_2^-, ClO_3^-, and ClO_4^-. What is the oxidation number of Cl atom in each species?

2. If you wanted to chrome plate a set of motorcycle exhaust pipes, should you be concerned that Cu^{2+} ions were also present, along with Cr^{3+} ions, in the electroplating bath?

3. MnO_4^{2-} undergoes disproportionation reaction in acidic medium but MnO_4^- does not. Give reason.

4. What is spectator ion? Give one example.

5. Consider the equation illustrating the decomposition of hydrogen peroxide:

$$2H_2O_2(aq) + 2H_2O(l) + O_2(g)$$

What has been oxidized and what has been reduced?

6. Consider the following set of reactions

$$N_2O_5 + 2NaHCO_3 \rightarrow 2NaNO_3 + 2CO_2 + H_2O$$
$$KClO_3 + 3HNO_2 \rightarrow KCl + 3HNO_3$$

Identify which of the reactions is a redox reaction and the compounds that are oxidized and reduced.

7. Define oxidation and reduction in terms of **(a)** electron transfer and **(b)** oxidation numbers.

8. How would you identify the oxidizing agent and reducing agent in a given reaction in terms of oxidation number?

9. Show that the formation of sodium chloride from gaseous sodium and gaseous chlorine is a redox reaction.

10. What are the maximum and minimum oxidation numbers of N, S and Cl?

11. Calculate the oxidation number of sulphur, chromium and nitrogen in H_2SO_5, $Cr_2O_7^{2-}$ and NO_3^-. Suggest structure of these compounds.

12. What sorts of information can you draw from the following reaction?

$$(CN)_2(g) + 2OH^- \rightarrow CN^-(aq) + CNO^-(aq) + H_2O(l)$$

13. Why is "loss of electrons" described as oxidation?

14. Laundry bleach is a dilute solution of sodium hypochlorite, NaOCl. Write a balanced net ionic equation for the reaction of NaOCl with $Na_2S_2O_3$. The OCl^- is reduced to chloride ion and the $S_2O_3^{2-}$ is oxidized to sulfate ion.

15. Use Table 2.2 to predict the outcome of the following reactions. If no reaction occurs, write N.R. If a reaction occurs, write a balanced chemical equation for it.

(A) $Fe + Mg^{2+} \rightarrow$ (B) $Cr + Pb^{2+} \rightarrow$
(C) $Ag^+ + Fe \rightarrow$ (D) $Ag + Au^{3+} \rightarrow$

16. It is observed that when magnesium metal is dipped into a solution of nickel(II) chloride, some of the magnesium dissolves and nickel metal is deposited on the surface of the magnesium. Which of the following reactions will occur spontaneously? Explain the reason for your answer.

(A) $2Mo^{3+} + 3Mg \rightarrow 3Mg^{2+} + 2Mo$
(B) $2Mo + 3Mg^{2+} \rightarrow 2Mo^{3+} + 3Mg$

17. The following chemical reactions are observed to occur in aqueous solution.

$$2AI + 3Cu^{2+} \rightarrow 2AI^{3+} + 3Cu$$
$$2AI + 3Fe^{2+} \rightarrow 3Fe + 2AI^{3+}$$
$$Pb^{2+} + Fe \rightarrow Pb + Fe^{2+}$$
$$Fe + Cu^{2+} \rightarrow Fe^{2+} + Cu$$
$$2AI + 3Pb^{2+} \rightarrow 3Pb + 2AI^{3+}$$
$$Pb + Cu^{2+} \rightarrow Pb^{2+} + Cu$$

18. A solution contains $Ce(SO_4)_3^{2-}$ at a concentration of 0.0150 M. It was found that in a titration, 25.00 mL of this solution reacted completely with 23.44 mL of 0.032 M $FeSO_4$ solution. The reaction gave Fe^{3+} as a product in the solution. In this reaction, what is the final oxidation state of the Ce?

19. Organic chemists often think about oxidation in terms of the loss of a pair of hydrogen atoms. Ethyl alcohol, CH_3CH_2OH, is oxidized to acetaldehyde CH_3CHO, for example, by removing a pair of hydrogen atoms. Show that this reaction obeys the general rule that oxidation is any process in which the oxidation number of an atom increases.

20. Differentiate between valency and oxidation number.

21. Give proper reasoning for the following

(A) An acidified potassium dichromate paper on being exposed to sulphur dioxide turns green.
(B) Iodide salts liberate iodine on addition of Cl_2 water.
(C) $HgCl_2$ and $SnCl_2$ cannot exist as such if present together in an aqueous solution.

22. The color of KI solution containing starch turns blue when it is shaken with cold Cl_2 water. Explain why?

23. Though alkaline potassium permanganate and acidic potassium permanganate both are used as oxidants, yet in the manufacture of benzoic acid from toluene we use alcoholic potassium permanganate as an oxidant. Why? Write a balanced redox equation for the reaction.

24. Chlorine is used to purify drinking water. Excess of chlorine is harmful. The excess of chlorine is removed by treating with sulphur dioxide. Present a balanced equation for this redox change taking place in water.

25. Give the balanced equations for the reactions that form the basis for the following redox titrations

(A) Titration of potassium permanganate for estimation of ferrous ions.
(B) Titration of iodine against sodium thiosulphate (iodimetric titration).
(C) Iodometric titration for estimation of cupric ions.

26. Define equivalent weight of an oxidizing/reducing agent.

27. Given the following $S_2O_3^{2-}(aq) \rightarrow SO_4^{2-}(aq)$, how many H^+ ions, and on which side of the $\rightarrow$ are required to balance the half reaction?

28. Identify the oxidants and reductants in the following reactions.

(A) $CH_4(g) + 4Cl_2(g) \rightarrow CCl_4(g) + 4HCl$

(B) $2H^+(aq) + MnO_2(s) + C_2H_2O_4 \rightarrow Mn^{2+}(aq) + 2CO_2(g) + 2H_2O(l)$

(C) $I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$

(D) $Cl_2(g) + 2Br^-(aq) \rightarrow 2Cl^-(aq) + Br_2(aq)$

29. What are half reactions? Explain with examples.

30. H_2O_2 acts as reductant as well as oxidant. Explain.

31. Balance the following equations in an acidic medium by both oxidation number and ion electron methods and identify the oxidants and reductants:

(A) $Bi(s) + NO_3^-(aq) \rightarrow Bi^{3+}(aq) + NO_2(g)$

(B) $H_2S(g) + Fe^{3+}(aq) \rightarrow Fe^{2+} + S(s) + H^+(aq)$

(C) $S(s) + HNO_3(aq) \rightarrow SO_2(g) + NO_2(g) + H_2O(l)$

(D) $As(s) + NO_3^-(aq) + H^+(aq) \rightarrow AsO_4^{3-}(aq) + NO_2(g) + H_2O(l)$

32. Identify the substances oxidized and reduced and the oxodizing and reducing agents in the reaction of **(a)** sodium with O_2; **(b)** aluminium with chlorine.

33. Balance equations for these reactions occurring in a basic solution.

(A) $CrO_4^{2-} + S^{2-} \rightarrow S + CrO_2^-$

(B) $MnO_4^- + C_2O_4^{2-} \rightarrow CO_2 + MnO_2$

(C) $ClO_3^- + N_2H_4 \rightarrow NO + Cl^-$

34. What is the oxidation state of Cl in **(a)** $HClO_4$, **(b)** $Ba(Cl_3)_2$, **(c)** CrO_2Cl_2 and **(d)** Cl_2O_7?

35. Indicate the species which are oxidized and reduced in the following reactions.

(A) $CN^- + OCl^- \rightarrow N_2 + HCO_3^- + Cl^-$

(B) $C_6H_5OH + O_3 \rightarrow CO_2 + H_2O + O_2$

(C) $I^- + O_3 \rightarrow O_2 + I_2$

(D) $S_2O_3^{2-} + Cl_2 \rightarrow HSO_4^- + Cl^-$

(E) $C + ZnO \rightarrow Zn + CO$

36. What is implied by the statement "oleum is labeled 109 % H_2SO_4"?

NUMERICAL PROBLEMS

1. 0.5 g of sample containing MnO_2 is treated with HCl, liberating Cl_2. The Cl_2 is passed into a solution of KI and 30.0 cm^3 of 0.1 M $Na_2S_2O_3$ are required to titrate the liberated iodine. Calculate the percentage of MnO_2 in sample (atomic weight of Mn = 55 u).

2. The neutralization of a solution of 1.2 g of mixture of $H_2C_2O_4 \cdot 2H_2O$ and $KHC_2O_4 \cdot H_2O$ and some impurities which are neutral, consumed 40.0 mL 0.25 N NaOH. On the other hand, on titration with $KMnO_4$, for a 0.4 g of mixture required 40.0 mL of 0.125 N $KMnO_4$. Find the percentage composition of mixture.

3. Iodate ion reacts with sulfite ion to give sulfate ion and iodide ion.

(A) Write a balanced net ionic equation for the reaction.

(B) How many grams of sodium sulfite are needed to react with 5.00 g of sodium iodate?

4. An organic compound contains carbon, hydrogen, and sulfur. A sample of it with a mass of 1.045 g was burned in oxygen to give gaseous CO_2, H_2O, and SO_2. These gases were passed through 500.0 mL of an acidified 0.0200 M $KMnO_4$ solution, which caused the SO_2 to be oxidized to SO_4^{2-}. Only part of the available $KMnO_4$ was reduced to Mn^{2+}. Next, 50.00 mL of 0.0300 M $SnCl_2$ was added to a 50.00 mL portion of this solution, which still contained unreduced $KMnO_4$. There was more than enough added $SnCl_2$ to cause all of the remaining MnO_4^- in the 50 mL portion to be reduced to Mn^{2+}. The excess Sn^{2+} that still remained after the reaction was then titrated with 0.0100 M $KMnO_4$, requiring 27.28 mL of the $KMnO_4$ solution to reach the end point. What was the percentage of sulfur in the original sample of the organic compound that had been burned?

5. How many mL of 0.05 M $KMnO_4$ is required to oxidize 2.0 g of $FeSO_4$ in dilute solution?

6. Metallic tin in presence of HCl is oxidized by $K_2Cr_2O_7$ to stannic chloride. What volume of decinormal dichromate solution will be reduced by 1g of tin? (Atomic weight of Sn = 118.7)

7. If 2.68×10^{-3} mol of a solution containing an ion A^{n+} require 1.61×10^{-3} moles of MnO_4^- for the oxidation of A^{n+} to AO_3^- in acid medium, what is the value of n?

8. Both $Cr_2O_7^{2-}(aq)$ and $MnO_4^-(aq)$ can be used to titrate $Fe^{2+}(aq)$. If in a given titration, 24.50 cm^3 of 0.1 M $Cr_2O_7^{2-}$ were used, then what volume of 0.1 M MnO_4^- solution would have been used for the same titration?

9. Ceric ammonium sulphate and potassium permanganate are used as oxidizing agents in the acidic medium for oxidation of ferrous ammonium sulphate to ferric sulphate. What is the ratio of the number of moles of cerium ammonium sulphate required per mole of ferrous ammonium sulphate to the number of moles of $KMnO_4$ required per mole of ferrous ammonium sulphate?

10. What is the number of moles of MnO_4^- required to oxidize one mole of ferrous oxalate completely in acidic medium?

11. An impure sample of sodium oxalate ($Na_2C_2O_4$) weighing 0.20 g is dissolved in aqueous solution of H_2SO_4 and solution is titrated at 70°C, requiring 45 mL of 0.02 M $KMnO_4$ solution. The end point is over-run, and back titration is carried out with 10 mL of 0.1 M oxalic acid solution. Find the % purity of $Na_2C_2O_4$ in sample.

12. A mixture of FeO and Fe_2O_3 is completely reacted with 100 mL of 0.25 M acidified $KMnO_4$ solution. The resultant solution was then titrated with Zn dust, which converted Fe^{3+} of the solution to Fe^{2+}. The Fe^{2+} required 1000 mL of 0.10 M $K_2Cr_2O_7$ solution. Find out the mass % Fe_2O_3 in the mixture.

13. A 150 mL of solution of I_2 is divided into two unequal parts. First part reacts with hypo solution in acidic medium. 15 mL of 0.4 M hypo was consumed. Second part was added with 100 mL of 0.3 M NaOH solution. Residual base required 10 mL of 0.3 M $H_2C_2O_4$ solution for complete neutralization. What was the initial concentration of I_2?

14. One gram of a sample of $CaCO_3$ was strongly heated and the CO_2 liberated was absorbed in 100 mL of 0.5 M NaOH. Assuming 90% purity for the sample, how much mL of 0.5 M HCl would be required to react with the solution of the alkali and $NaCO_3$ to reach the phenolphthalein end point?

15. The concentration of bivalent lead ions in a sample of polluted water that also contains nitrate ions is determined by adding solid sodium sulphate ($M_B = 142$ g mol^{-1}) to exactly 500 mL of water. Calculate the molarity of lead ions if 0.355 g of sodium sulphate was needed for complete precipitation of lead ions as sulphate.

16. One liter of a mixture of O_2 and O_3 at NTP were allowed to react with an excess of acidified solution of KI. The iodine liberated required 40 mL of M/10 sodium thiosulphate solution for titration. Knowing that ultraviolet radiations of wavelength 300 nm can decompose ozone and assuming that one photon can decompose one molecule of ozone, what is the number of photons required for the complete decomposition of ozone in the original mixture?

17. Gastric juice contains about 3.0 g of HCl per liter. If a person produces about 2.5 L of gastric juice per day, how many antacid tablets each containing 400 mg of $Al(OH)_3$ are needed to neutralize all the HCl produced in one day?

18. 20 mL of a solution containing 0.2 g of impure sample of H_2O_2 reacts with 0.316 g of $KMnO_4$ in presence of H_2SO_4 as per following reaction.

$$KMnO_4 + H_2O_2 + H_2SO_4 \rightarrow MnSO_4 + O_2 + H_2O$$

(A) Find the purity of H_2O_2 solution
(B) Calculate the volume of dry oxygen evolved at 27°C and at 750 mm Hg.

19. Borax in water gives:

$$B_4O_7^{2-} + 7H_2O \rightarrow 4H_3BO_3 + 2OH^-$$

How many grams of borax ($Na_2B_4O_7 \cdot 10H_2O$) are required to:
(A) Prepare 50 mL of 0.2 M solution
(B) Neutralize 25 mL of 0.1934 M of MCl and H_2SO_4 separately

20. Consider 2.36 g of sample of dolomite containing only $CaCO_3$ and $MgCO_3$ to be dissolved in 700 mL of 0.1 N HCl. The solution was diluted to 2.5 L, 25 mL of this solution required 20 mL of 0.01 N NaOH solution for complete neutralization. Find the percentage composition of the ore.

21. When 12.49 g of a sample of pure $BaCO_3$ and impure $CaCO_3$ containing some CaO was treated with dil. HCl, it evolved 168 mL of CO_2 at NTP. From this solution, $BaCrO_4$ was precipitated, filtered and washed. The precipitate was dissolved in dilute sulphuric acid and diluted to 100 mL. When 10 mL of this solution was treated with KI solution, iodine was liberated which required exactly 20 mL of 0.5 N $Na_2S_2O_3$. Calculate the percentage of CaO in the sample.

ADDITIONAL OBJECTIVE QUESTIONS

Single Correct Choice Type

1. In the reaction, $Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + NaI$ (not balanced), which of the following is/are true?
(I) $Na_2S_2O_3$ is a reducing agent.
(II) Iodine is an oxidizing agent.
(III) It is an example of intermolecular redox reaction.
(IV) In $Na_2S_4O_6$ the average oxidation state of S is (+5/2)
(A) I, II, IV
(B) I, II
(C) I, II, III
(D) I, II, III, IV

2. The number of electrons involved in the reduction of nitrate ion (NO_3^-) to hydrazine (N_2H_4) is
(A) 8
(B) 7
(C) 5
(D) 3

3. SO_2 under atmospheric condition changes to SO_x^{2-}. If oxidation number of S in is + 6, what is the value of x in SO_x^{2-}?
(A) 1
(B) 2
(C) 3
(D) 4

4. $NaIO_3$ reacts with $NaHSO_3$ according to equation: $IO_3^- + 3HSO_3^- \rightarrow I^- + 3H^+ + 3SO_4^{2-}$. The weight of $NaHSO_3$ required to react with 100 mL of solution containing 0.66 g of $NaIO_3$ is
(A) 5.2 g
(B) 4.57 g
(C) 2.3 g
(D) 10.4 g.

5. In the reaction $4I^- + Hg^{2+} \rightarrow HgI_4^{2-}$, 1 mol each of Hg^{2+} and I^- will form
(A) 1 mol
(B) 0.5 mol
(C) 0.25 mol
(D) 2 mol

6. A 0.46 g sample of As_2O_3 required 25.0 ml of $KMnO_4$ solution for its titration. The molarity of $KMnO_4$ solution is
(A) 0.016
(B) 0.064
(C) 0.032
(D) 0.128

7. Number of moles of $K_2Cr_2O_7$ reduced by 1 mole of Sn^{2+} is
(A) 1/3
(B) 1/6
(C) 2/3
(D) 1

8. Equivalent weight of H_3PO_2 (mol. wt. = M) when it disproportionates into PH_3 and H_3PO_3 is
(A) M
(B) M/2
(C) M/4
(D) 3M/4

9. Amongst the following, identify the species with an atom in +6 oxidation state.
(A) MnO_4^-
(B) $Cr(CN)_6^{3-}$
(C) NiF_6^{2-}
(D) CrO_2Cl_2

10. What is the equivalent weight of $C_{12}H_{22}O_{11}$ in the following reaction?

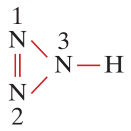
$C_{12}H_{22}O_{11} + 36\ HNO_3 \rightarrow 6\ H_2C_2O_4 + 36\ NO_2 + 23\ H_2O$

(A) 342/36
(B) 342/12
(C) 342/22
(D) 342/3

11. Which oxyacid of Cl cannot undergo disproportionation?
(A) HClO
(B) $HClO_2$
(C) $HClO_3$
(D) $HClO_4$

12. Which of the following oxides is most basic?
(A) MnO
(B) Mn_2O_3
(C) MnO_2
(D) Mn_2O_7

13. In this compound HN_3 (hydrazoic acid), oxidation state of N^1, N^2 and N^3 are



(A) 0, 0, 3
(B) 0, 0, –1
(C) 1, 1, –3
(D) –3, –3, –3

14. Which of the following agents is the most oxidizing?
(A) O_3
(B) $KMnO_4$
(C) H_2O_2
(D) $K_2Cr_2O_7$

15. When 1 mol of $KClO_3$ takes 4 mol of electrons, the expected product is
(A) ClO^{2-}
(B) ClO^{4-}
(C) OCl
(D) Cl^-

16. On the basis of structure, the oxidation states of two Cl atoms in $CaOCl_2$, respectively, are
(A) –1 and +1
(B) +2 and –2
(C) –2 and +2.
(D) –1 and +3.

17. A blue color appears on addition of aqueous ammonia to aqueous $CuSO_4$ due to reaction

$$CuSO_4 + 4NH_3 \rightarrow [Cu(NH_3)_4]SO_4$$

In this reaction,
(A) copper is oxidized.
(B) copper is reduced.
(C) ammonia is reduced.
(D) None of these.

18. Among the following molecules, in which does bromine show the maximum oxidation number?
(A) $Hg_2(BrO_3)_2$
(B) Br–Cl
(C) $KBrO_4$
(D) Br_2

19. When copper is treated with a certain concentration of nitric acid, nitric oxide and nitrogen dioxide are liberated in equal volumes according to the equation,

$$x\text{Cu} + y\text{HNO}_3 \rightarrow Cu(NO_3)_2 + NO + NO_2 + H_2O.$$

The coefficients of x and y are
(A) 2 and 3
(B) 2 and 6
(C) 1 and 3
(D) 3 and 8

20. What is the oxidation number of carbon in A?

$$CH_2(COOH)_2 \xrightarrow{P_4O_{10}} A$$

(A) +4
(B) +3/4
(C) +4/3
(D) +2/3

21. When iodine is passed through sodium thiosulphate, it is decolorized and sodium tetrathionate is formed. What is the change in the oxidation number of a sulphur atom in the reaction?
(A) 1/2
(B) 3/2
(C) 2
(D) 1

22. In the alkaline medium, the color of potassium dichromate solution changes from orange to yellow due to the formation of potassium chromate. What is the change in oxidation state of chromium?
(A) 1
(B) 2
(C) 3
(D) 0

23. The oxidation number of carbon in CH_2Cl_2 is
(A) –4
(B) +4
(C) 0
(D) –2

24. SO_2 is passed through an acidified solution of potassium dichromate, the oxidation state of S changes from
(A) +4 to 0
(B) +4 to +2
(C) +4 to +6
(D) +6 to +4

25. The oxidation states of sulphur in the anions SO_3^{2-}, $S_2O_4^{2-}$ and $S_2O_6^{2-}$ follow the order
(A) $S_2O_4^{2-} < SO_3^{2-} < S_2O_6^{2-}$
(B) $SO_3^{2-} < S_2O_4^{2-} < S_2O_6^{2-}$
(C) $S_2O_4^{2-} < S_2O_6^{2-} < SO_3^{2-}$
(D) $S_2O_6^{2-} < S_2O_4^{2-} < SO_3^{2-}$

26. Which of the following compounds contain the metal atom in its highest possible oxidation state?
(A) KSCN
(B) MnO_2
(C) Cr_2O_3
(D) H_2SnCl_4

27. A compound of Xe and F is found to have 53.5% Xe. What is the oxidation number of Xe in this compound?
(A) –4
(B) 0
(C) +4
(D) +6

28. Which reaction involves neither oxidation nor reduction?
(A) $CrO_4^{2-} \rightarrow Cr_2O_7^{2-}$
(B) $Cr \rightarrow CrCl_3$
(C) $Na \rightarrow Na^+$
(D) $2S_2O_3^{2-} \rightarrow S_4O_6^{2-}$

29. Which one of the following is an example of disproportionation?
(A) $NH_3 + 3CuO \rightarrow 3Cu + 3H_2O + N_2$
(B) $5HI + HIO_3 \rightarrow 3H_2O + 3I_2$
(C) $I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6$
(D) $P_4 + 3NaOH + 3H_2O \rightarrow 3NaH_2PO_2 + PH_3$

30. H_2O_2 acts as a reducing agent in
(A) $2 + HCl + H_2O_2 \rightarrow FeCl_3 + H_2O$
(B) $Cl_2 + H_2O_2 \rightarrow 2HCl + O_2$
(C) $2HI + H_2O_2 \rightarrow I_2 + H_2O$
(D) $H_2SO_3 + H_2O_2 \rightarrow H_2SO_4 + H_2O$

31. Which of the following has been arranged in order of increasing oxidation number of nitrogen?
(A) $NH_3 < N_2O_5 < NO < N_2$
(B) $NO_2^+ < NO_3^- < NO_2^- < N_3^-$
(C) $NH_4^+ < N_2H_4 < NH_2OH < N_2O$
(D) $NO_2 < NaN_3 < NH_4^+ < N_2O$

32. Which of the following agents is the most reducing?
(A) Mg
(B) Na
(C) K
(D) Br_2

33. No disproportionation is possible for
(A) AsH_3
(B) SF_4
(C) H_5IO_6
(D) PCl_3

34. In the reaction

$$3Br_2 + 6CO_3^{2-} + 3H_2O \rightarrow 5Br^- + BrO_3^- + 6HCO_3^-$$

(A) bromine is oxidized and carbonate is reduced.
(B) bromine is reduced and water is oxidized.
(C) bromine is neither reduced nor oxidized.
(D) bromine is both reduced and oxidized.

35. When the ion $Cr_2O_7^{2-}$ acts as an oxidant in the acidic aqueous solution, the ion Cr^{3+} is formed. How many moles of Sn^{2+} would be oxidized to Sn^{4+} by one mol of $Cr_2O_7^{2-}$ ions?
(A) 1
(B) 2
(C) 4
(D) 3

36. A sample of 2.5 mol of hydrazine (N_2H_4) loses 25 mol of electrons on being converted to a new compound X. Assuming that there is no loss of nitrogen in the formation of the new compound, what is the oxidation number of nitrogen in compound X?
(A) −1
(B) −2
(C) +3
(D) +4

37. An element, which never has a positive oxidation state in any of its compounds, is
(A) boron.
(B) oxygen.
(C) chlorine.
(D) fluorine.

38. The average oxidation number of sulphur in $Na_2S_4O_6$ is
(A) 1.5
(B) 2.5
(C) 3
(D) 2

39. Oxidation number of fluorine in F_2O is
(A) +1
(B) +2
(C) −1
(D) −2

40. How many moles of $KMnO_4$ are required in the acidic medium for complete oxidation of 15 mol of $FeSO_4$?
(A) 2
(B) 3
(C) 4
(D) 5

41. Equivalent weight of MnO_4^- in acidic, basic, and neutral media is in the ratio of
(A) 3:5:15
(B) 5:3:1
(C) 5:1:3
(D) 3:15:5

42. Sulphur has highest oxidation state in
(A) H_2SO_4
(B) SO_2
(C) $Na_2S_2O_3$
(D) $Na_2S_4O_6$

43. In which of the following compounds, transition metal has zero oxidation state?
(A) CrO_5
(B) $NH_2 \cdot NH_2$
(C) $NOClO_4$
(D) $[Fe(CO)_5]$

44. Consider the following reactions:

(I) $C_2O_4^{2-} \rightarrow CO_2$
(II) $SO_4^{2-} \rightarrow SO_3^{2-}$
(III) $MnO_4^{2-} \rightarrow MnO_4^+$
(IV) $Fe^{3+} \rightarrow Fe^{2+}$

Choose the correct answer:
(A) (I) and (II) show oxidation.
(B) (III) and (IV) shows reduction.
(C) (I) and (III) show oxidation.
(D) (III) and (IV) shows oxidation.

45. In the reaction $Cl_2 + OH^- \rightarrow Cl^- + ClO_3^- + H_2O$, chlorine is
(A) oxidized.
(B) reduced.
(C) oxidized as well as reduced.
(D) neither oxidized nor reduced.

46. How many moles of electron is needed for the reduction of each mole of Cr in the following reaction?

$$CrO_5 + H_7SO_4 \rightarrow Cr_2(SO_4)_3 + H_2O + O_2$$

(A) 4
(B) 3
(C) 5
(D) 7

47. Hydroxylamine reduces iron(III) according to following equation

$$NH_2OH + Fe_2(SO_4)_3 \rightarrow N_2(g) + H_2O + FeSO_4 + H_2SO_4$$

Which statement is correct?
(A) *n*-factor for hydroxylamine is 1.
(B) Equivalent weight of $Fe_2(SO_4)_3$ is M/2.
(C) 6 Milliequiv. of $Fe_2(SO_4)_3$ is contained in 3 millimoles of ferric sulphate.
(D) All of these.

48. Equal volumes of 1 M each of $KMnO_4$ and $K_2Cr_2O_7$ are used to oxidize Fe(II) solution in acidic medium. The amount of Fe oxidized will be
(A) more with $KMnO_4$.
(B) more with $K_2Cr_2O_7$.
(C) equal with both oxidizing agents.
(D) cannot be determined.

49. What volume of 1 M FeC_2O_4 (ferrous oxalate) solution is required for the complete oxidation of 100 mL of 1 M $Fe(SCN)_2$ solution into Fe^{3+}, SO_4^{2-}, CO_4^{2-} and nitrate ?
(A) 0.7 L
(B) 1 L
(C) 0.8 L
(D) 1.1 L

50. A solution contains Cu^{2+} and $C_2O_4^{2-}$ ions which on titration with 1 M $KMnO_4$ consumes 10 mL of the oxidizing agent for complete oxidation in acidic medium. The resulting solution is neutralized with Na_2CO_3, acidified with dil. CH_3COOH and is treated with excess of KI. The liberated iodine requires 25 mL of 1 M of hypo solution, then that will be the molar ratio of Cu^{2+} to $C_2O_4^{2-}$ ions in solution?
(A) 5 : 2 (B) 1 : 2
(C) 2 : 1 (D) 1 : 1

51. The labeling on a bottle of H_2O_2 solution is 20 "vol," then the concentration of H_2O_2 in percentage strength will be:
(A) 3.03% (B) 5%
(C) 4.55% (D) 6.06%

52. A 100 mL solution of 0.1 N HCl was titrated with 0.2 N NaOH solution. The titration was discontinued after adding 30 mL of NaOH solution. The remaining titration was completed by adding 0.25 N KOH solution. The volume of KOH required for completing the titration is
(A) 70 mL (B) 32 mL
(C) 35 mL (D) 16 mL

53. 40% *w*/*V* NaCl solution (specific gravity = 1.12) is equivalent to
(A) 3.57×10^5 ppm (B) 3.57×10^6 ppm
(C) 1×10^6 ppm (D) 4×10^5 ppm

54. Oxalic acid ($H_2C_2O_4$) form two series of salt $HC_2O_4^-$ and $C_2O_4^-$. If 0.9 g of oxalic acid is in 100 mL solution, $HC_2O_4^-$ and $C_2O_4^-$ have normality, respectively,,
(A) 0.1 N, 0.1N (B) 0.1 N, 0.2 N
(C) 0.2 N, 0.2 N (D) 0.2 N, 0.1 N

Multiple Correct Choice type

1. $H_2C_2O_4$ and $NaHC_2O_4$ behave as acids as well as reducing agents. Which are correct statements?
(A) Equivalent weight of $H_2C_2O_4$ and $NaHC_2O_4$ are equal to their molecular weights when acting as reducing agents
(B) Equivalent weight of $H_2C_2O_4$ and $NaHC_2O_4$ are equal to half their molecular weights when acting as reducing agents
(C) 100 mL of 1 M solution of each is neutralized by equal volumes of 1 N $Ca(OH)_2$
(D) 100 mL of 1 M solution of each is oxidized by equal volumes of 1 M $KMnO_4$

2. For the following balanced redox reaction,

$$2MnO_4^+ + 4H^+ + Br_2 \rightleftharpoons 2Mn^{2+} + 2BrO_3^+ + 2H_2O$$

If the molecular wt. of MnO_4^-, Br_2 be M_x, M_y, respectively, then
(A) equivalent weight of MnO_4^+ is $M_x/5$.
(B) equivalent weight of Br_2 is $M_y/10$.
(C) the *n*-factor ratio of Mn^{2+} to BrO_3^- is 1 : 1.
(D) none of these.

3. Which of the following statements about the following reactions are wrong?

$$2Cu_2O(s) + Cu_2S(s) \rightarrow 6Cu(s) + SO_2g$$

(A) Both Cu_2O and Cu_2S are reduced.
(B) Only Cu_2S is reduced.
(C) Cu_2S is the oxidant.
(D) Only Cu_2O is reduced.

4. Which of the following substances undergo disproportionation reactions under basic medium?
(A) F_2 (B) P_4
(C) S_8 (D) Br_2

5. A reducing agent in a redox reaction undergoes
(A) a decrease in oxidation number.
(B) an increase in oxidation number.
(C) loss of electrons.
(D) gain of electrons.

6. Which of the following statements are correct?
(A) All reactions are oxidation and reduction reactions.
(B) Oxidizing agent is itself reduced.
(C) Oxidation and reduction always go side by side.
(D) Oxidation number during reduction decreases.

7. The metals undergoing disproportionation are
(A) Sn (B) Na
(C) Cu (D) Ca

8. Which of the following is correct about acidic nature?
(A) $H_3PO_4 > H_3PO_3$ (B) $H_3AsO_4 > H_3AsO_3$
(C) $HClO_4 > HClO_3$ (D) $HNO_3 > HNO_2$

9. In which of the following, oxidation number of oxygen is fractional?
(A) B_4O_{10} (B) B_2H_6
(C) CsO_2 (D) KO_3

10. The reaction $KI + I_2 \rightarrow KI_3$ is
(A) oxidation. (B) reduction.
(C) complex formation. (D) None of these.

11. The activity series of metals is
$Au < Ag < Cu < Sn < Cd < Zn < Al < Mg < Na < Cs$
Which reaction below **does not** occur spontaneously upon mixing the reagents shown?
(A) $Cd(s) + Al^{3+}(aq) \rightarrow Cd^{2+}(aq) + Al(s)$
(B) $Cd(s) + Cu^{2+}(aq) \rightarrow Cd^{2+}(aq) + Cu(s)$
(C) $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$
(D) $Al(s) + Ag^{+}(aq) \rightarrow Al^{3+}(aq) + Ag(s)$

12. Which of the following represent redox reactions?
(A) $Cr_2O_7^{2-} + 2OH^- \rightarrow 2CrO_4^{2-} + H_2O$
(B) $2CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$
(C) $2MnO_4 + 3Mn^2 + 4OH^- \rightarrow 5MnO_2 + 2H_2O$
(D) $IO_4^- + I^- + H^+ \rightarrow I_2 + H_2O$

13. For the following balanced redox reaction,

$$2MnO_4^+ + 4H^+ + Br_2 \rightleftharpoons 2Mn^{2+} + 2BrO_3^+ + 2H_2O$$

If the molecular weight of MnO_4^-, Br_2 be M_{B1}, M_{B2}, respectively, then
(A) equivalent weight of MnO_4^- is $M_{B1}/5$.
(B) equivalent weight of Br_2 is $M_{B2}/10$.
(C) the *n*-factor ratio of Mn^{2+} to BrO_3^- is 1:1.
(D) none of these.

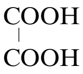
14. When non-stoichiometric compound $Fe_{0.95}O$ is heated in presence of oxygen, then it converts into Fe_2O_3. Which of the following statements are correct?
(A) Equivalent weight of $Fe_{0.95}$ O is $M_B/0.5$ where M_B is molecular weight of $Fe_{0.95}O$.

(B) The number of moles of Fe^{3+} and Fe^{2+} in 1 mol $Fe_{0.95}O$ are 0.1 and 0.85, respectively.
(C) The number of moles of Fe^{3+} and Fe^{2+} in 1 mol of $Fe_{0.95}O$ are 0.85 and 0.1, respectively
(D) The % composition of Fe^{2+} and Fe^{3+} in the non-stoichiometric compound is 89.47% and 10.53%, respectively.

15. A group of students attempted to estimate the concentration of Fe^{2+} by pipetting fixed volumes of the solution into a flask, adding an excess of dilute sulphuric acid, and then titrating with a standard solution of potassium manganate (VII) from a burette. The volume of $KMnO_4$ solution required by one student was 0.2 cm^3 higher than that of the other students. Which of the following are possible explanations for this discrepancy?
(A) The titration flask was rinsed with the solution of Fe^{2+} instead to water before titration.
(B) The last drop of Fe^{2+} solution was blown from the pipette into the flask.
(C) The burette was rinsed with water instead of the solution of $KMnO_4$ before titration.
(D) One student rinsed with the solution of Fe^{2+} and other rinsed with solution of $KMnO_4$ before titration.

16. 40 g NaOH, 106 g Na_2CO_3 and 84 g. $NaHCO_3$ is dissolved in water and the solution is made 1 L, 20 mL of this stock solution is titrated with 1 N HCl, hence which of the following statements are correct?
(A) The liter reading of HCl will be 40 mL, if phenolphthalein is used indicator from the very beginning.
(B) The liter reading of HCl will be 60 mL if phenolphthalein is used indicator from the very beginning.
(C) The liter reading of HCl will be 40 mL if methyl orange is used indicator after the first end point.
(D) The liter reading of HCl will be 80 mL, if methyl orange is used as indicator from the very beginning.

17. 150 mL of M/10 $Ba(MnO_4)_2$ in acidic can oxidize completely
(A) 150 mL of 1 M Fe^{2+} solution.
(B) 50 mL of 1 M FeC_2O_4 solution.
(C) 75 mL of 1 M $C_2O_4^{2-}$ solution.
(D) 25 mL of 1 M $K_2Cr_2O_7$ solution.

18.  $\begin{array}{c}\text{COOH}\\|\\\text{COOH}\end{array}$ and $\begin{array}{c}\text{COOK}\\|\\\text{COOH}\end{array}$ behave as acids are well as reducing agents. Then which of the following are the correct statements?
(A) When they behave as reducing agents, then their equivalent weights are equal to half of their molecular weights, respectively.
(B) 1000 mL of 1 N solution of each is neutralized by 1000 mL 1 N $Ca(OH)_2$.
(C) 1000 mL of 1 M solution of each is neutralized by 1000 mL of 1 M $Ca(OH)_2$.
(D) 1000 mL of 1 M solution of each is neutralized by 200 mL 2 M of $KMnO_4$ in acidic medium.

19. 0.1 mol of MnO_4^- (in acidic medium) can
(A) oxidize 0.5 mol of Fe^{2+}
(B) oxidize 0.166 mol of FeC_2O_4
(C) oxidize 0.25 mol of $C_2O_4^{2-}$
(D) oxidize 0.6 mol of $Cr_2O_7^{2-}$

20. The reaction $3ClO^-(aq) \rightarrow ClO_3^-(aq) + 2Cl^-(aq)$ is an example of
(A) oxidation reaction.
(B) reduction reaction.
(C) disproportionation reaction.
(D) decomposition reaction.

Assertion–Reasoning Type

Choose the correct option from the following:
(A) Statement 1 is True, Statement 2 is True; Statement 2 is a correct explanation for Statement 1.
(B) Statement 1 is True, Statement 2 is True; Statement 2 is NOT a correct explanation for Statement 1.
(C) Statement 1 is True, Statement 2 is False.
(D) Statement 1 is False, Statement 2 is True.

1. **Statement 1:** The equivalent weight of reducing agent, Fe^{2+} is 56 (atomic mass of Fe = 56).

Statement 2: Fe loses $2e^-$ to be converted into Fe^{2+}.

2. **Statement 1:** In the roasting of FeS_2, ore is converted into ferric oxide and SO_2 gas. The equivalent mass of FeS_2 is equal to molecular weight/11.

Statement 2: The *n*-factor for reducing agent is total net change in oxidation number per formula unit.

3. **Statement 1:** In CrO_5, there must be peroxide linkage. **Statement 2:** The maximum oxidation number of an element cannot exceed its number of valence electron.

4. **Statement 1:** $CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2$ is a redox reaction.

Statement 2: Equivalent weight of $CaCO_3$ in this reaction is 50.

5. **Statement 1:** Fe reacts with HCl to produce H_2 gas.

Statement 2: Fe is a better reducing agent than H_2.

6. **Statement 1:** Hydrogen peroxide acts only as oxidizing agent.

Statement 2: All peroxides can undergo disproportionation.

7. **Statement 1:** Oxidation number of carbon in HCN is +2.

Statement 2: Carbon always shows an oxidation state of +4.

8. **Statement 1:** When $SnCl_2$ solution is added to $HgCl_2$ solution, a milky white precipitate is obtained and on adding excess $SnCl_2$, a black precipitate is formed.

Statement 2: The disproportionation of Hg(II) is easier than its reduction only.

9. **Statement 1:** Iodine shows oxidation state of +1 and +3 in the compounds ICl and ICl_3, respectively.

Statement 2: Iodine coming below the halogens F, Cl, Br in the halogen group of elements in the periodic table shows a higher degree of electropositive nature.

10. **Statement 1:** In aqueous solution, SO_2 reacts with H_2S liberating sulphur.

Statement 2: SO_2 is an effective reducing agent.

11. **Statement 1:** In the titrations of Na_2CO_3 with HCl using methyl orange indicator, the volume required at the equivalence point is twice that of acid required using phenolphthalein indicator.

Statement 2: Two moles of HCl are required for complete neutralization of one mole of Na_2CO_3.

12. **Statement 1:** The equivalent weight of reducing agent, Fe^{2+} is 56 (atomic mass of Fe = 56).

Statement 2: Fe loses $2e^-$ to be converted into Fe^{2+}.

13. **Statement 1:** Equivalent weight of a species can be written as molecular weight of the species divided by valence factor.

Statement 2: Valence factor represents valence in element, acidity in bases, basicity in acids and total charge on cation or anion in an ionic compound

14. **Statement 1:** In solution A(200 mL of 0.1 N HCl) and solution B(100 mL of 0.2 N HCl), the equivalents of H^+ are the same.

Statement 2: Number of equivalents = Normality × Volume (in liter).

15. **Statement 1:** Addition of water to a solution containing solute and solvent changes its normality or molarity.

Statement 2: The milliequivalents and millimoles of the solute are not changed on dilution.

Comprehension Type

Read the paragraphs and answer the questions that follow.

Paragraph I

Aqueous solution of sodium hypochlorite (NaOCl) is a household bleach and a strong oxidizing agent that reacts with chromite ion $[Cr(OH)_4]^-$ in basic solution to yield chromate (CrO_4^{2-}) and chloride ion.

1. Select the correct statement(s)

(A) OCl^- has been oxidized and $[Cr(OH)_4]^-$ has been reduced.

(B) OCl^- has been reduced and $[Cr(OH)_4]^-$ has been oxidized.

(C) It is simply a neutralization reaction

(D) It is simply a displacement reaction

2. Balanced equation (only redox species) is

(A) $ClO^- + [Cr(OH)_4]^- \rightarrow CrO_4^{2-} + Cl^-$

(B) $3ClO^- + [Cr(OH)_4]^- \rightarrow CrO_4^{2-} + 3Cl^-$

(C) $3ClO^- + 2[Cr(OH)_4]^- \rightarrow 2CrO_4^{2-} + 3Cl^-$

(D) $ClO^- + 2[Cr(OH)_4]^- \rightarrow 2CrO_4^{2-} + Cl^-$

Paragraph II

For the unbalanced reaction $AX + BY + H_2O \rightarrow HA + OY + X_2B$. Let the oxidation number of X be –2 and X, H_2O are not involved in redox reaction.

3. The element(s) undergoing oxidation is

(A) A (B) B
(C) Y (D) Both B and Y

4. The possible oxidation states of B and Y in BY are, respectively,

(I) +1, –1 (II) +2, –2
(III) +3, –3

(A) I (B) II
(C) III (D) I, II, III

5. If the above reaction is balanced in acid medium, the sum of smallest whole number stoichiometric coefficients of all the compounds will be

(A) 9 (B) 8
(C) 7 (D) 6

Paragraph III

Electron transfer or redox reactions involve simultaneous reduction and oxidation reactions. A substance is reduced when it gains electrons, and if it loses electrons it is said to be oxidized. A substance brings out reduction of other substances is called reducing agent, and the one which brings out oxidation of other substances is called oxidizing agent. In disproportionation, the same substance undergoes both oxidation and reduction. Two identical components of same molecule or different molecule undergo oxidation and reduction to result a common product in this reaction called comproportionation reaction.

6. $2MnO_4^{2-} + 2H_2O \rightarrow MnO_2 + 2MnO_4^- + 4OH^-$ is an example of

(A) intermolecular redox reaction.

(B) intramolecular redox reaction.

(C) disproportionation reaction.

(D) comproportionation reaction.

7. Which among the following is not a disproportionation reaction?

(A) $P_4 + OH^- \rightarrow H_2PO_4^- + PH_3$

(B) $S_2O_3^{2-} \rightarrow SO_4^{2-} + S$

(C) $H_2O_2 \rightarrow H_2O + O_2$

(D) $AgCl + NH_3 \rightarrow [Ag(NH_3)_2]Cl$

8. In the reaction $MnO_4^{2-} + 2H_2O + 2e^- \rightarrow MnO_2 + 4OH^-$, MnO_2, will act as

(A) an oxidizing agent.

(B) reducing agent.

(C) both as an oxidizing and reducing agent.

(D) precipitating agent.

Paragraph IV

A sample of iron(II) sulphate crystals, $FeSO_4 \cdot 7H_2O$ has been left open to the air and some of the iron(II) ions has been converted to iron(III). 4.2 g of the impure crystals were dissolved in a total of 250 cm^3 water and dilute sulphuric acid. 25 cm^3 portion of this solution was titrated with a solution of potassium bicarbonate(VI). The concentration of dichromate(VI) ions in this solution was 0.1 mol dm^{-3}. The average volume used was 23.5 cm^3.

9. How many moles of Fe^{2+} ions would there have been in the 250 cm^3 of stock solution?

(A) 7.05×10^{-4} mol (B) 2.35×10^{-4} mol
(C) 1.41×10^{-2} (D) 7.05×10^{-4} mol

10. What mass of Fe^{2+} ions should have been present in the 4.2 g of crystals?

(A) 0.84 g (B) 0.90 g
(C) 0.77 g (D) 0.62 g

11. The percentage purity of the crystal is

(A) 69% (B) 72%
(C) 88% (D) 94%

Paragraph V

1.00 g of a mixture having equal number of moles of carbonates of two alkali metals required 44.4 mL of 0.5 N HCl for complete reaction. Atomic weight of one of the metals is 7.00.

12. The number of moles of each metal carbonate is
(A) 0.1 (B) 0.0111
(C) 0.0055 (D) 0.00275

13. The number of equivalents of HCl used is
(A) 0.222 (B) 2.22
(C) 22.22 (D) 0.0222

Paragraph VI

Iodine titrations can be iodometric or iodimetric depending on using iodine directly or indirectly as an oxidizing agent in the redox titration.

(a) Iodimetric titrations in which a standard iodine solution is used as an oxidant and iodine is directly titrated against a reducing agent. For example,

$$2CuSO_4 + 4KI \rightarrow Cu_2I_2 + 2K_2SO_4 + I_2$$

(b) Iodimetric procedures are used for the determination of strength of reducing agent such as thiosulphates, sulphites, arsenites and stannous chloride, etc., by titrating them against standard solution of iodine taken in a burette

$$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$$

Starch is used as indicator near the end point which from blue color complex with I_3^-. The blue color disappears when there is not more of free I_2.

14. In the reaction $2CuSO_4 + 4KI \rightarrow Cu_2I_2 + 2K_2SO_4 + I_2$, the equivalent weight of $CuSO_4$ is (M_B: molecular weight)
(A) $M_B/8$ (B) $M_B/4$
(C) $M_B/2$ (D) M_B

15. The volume of KI solution used for $CuSO_4$ will be
(A) 100 mL (B) 40 mL
(C) 400 mL (D) 200 mL

16. When 319.0 g of $CuSO_4$ in a solution is reacted with excess of 0.5 M KI solution, then liberated iodine required 100 mL of 1.0 M $Na_2S_2O_3$ for complete reaction. The percentage purity of $CuSO_4$ in the sample is
(A) 10% (B) 20%
(C) 5% (D) none of these

Paragraph VII

Oleum is a mixture of H_2SO_4 and SO_3 (i.e., $H_2S_2O_7$). It is produced by passing SO_3 in H_2SO_4 solution. In order to dissolve free SO_3 in oleum, dilution of oleum is done, in which oleum converts into pure H_2SO_4. It is shown by the reaction as under:

$$H_2SO_4 + SO_3 + H_2O \rightarrow 2\ H_2SO_4\ \text{(pure)}$$

$$SO_3 + H_2O \rightarrow H_2SO_4\ \text{(pure)}$$

When 100 g sample of oleum is diluted with desired amount of H_2O (in g), then the total mass of pure H_2SO_4 obtained after dilution is known as percentage labeling in oleum. Through this process, the percentage composition of H_2SO_4, SO_3 (free) and SO_3 (combined) is calculated.

If oleum sample is labeled as "109% H_2SO_4," that is, 100 g of oleum on dilution with 9 g of H_2O provides 109 g pure H_2SO_4, in which all free SO_3 in 100 g of oleum is dissolved.

17. For 109% labeled oleum, if the number of moles of H_2SO_4 and free SO_3 be x and y, respectively, then what will be the value of $x^2 + y^2$?
(A) 0.15 (B) 0.42
(C) 0.62 (D) 0.80

18. The percentage of combined SO_3 in the given oleum sample is
(A) 20% (B) 30%
(C) 48.98% (D) 51 %

19. The percentage composition of free SO_3 and H_2SO_4 in the oleum sample, respectively, are
(A) 60%, 40% (B) 30%, 70%
(C) 85%, 15% (D) 40%, 60%

20. What volume of 1 M NaOH (in mL) will be required to react completely with H_2SO_4 and SO_3?
(A) 250 mL (B) 2224 mL
(C) 750 mL (D) 1800 mL

Integer Answer Type

The answer is a **non-negative integer**.

1. The number of electrons involved in the conversion of MnO_4^- to MnO_2 is ______.

2. In $Ba(H_2PO_2)_2$ the oxidation number of phosphorus is ______.

3. In bleaching powder ($CaOCl_2$), the oxidation states of chlorine are x and y. The value of $x + y$ is ______.

4. Given balanced chemical equation for oxidation of phosphorus (III) sulphide by nitric acid. The products include NO and SO_2. The reaction is

$$aP_4S_6 + bH^+ + cNO_3^- \rightarrow dNO + eH_3PO_4 + fSO_2 + gH_2O$$

What is the value of $(a + g)$?

5. In the redox reaction,

$$xNO_3^- + yAs_2S_3 + zH_2O \rightarrow AsO_4^{3-} + NO^+ + SO_4^{2-} + H^+$$

what is the value of (x/z)?

6. Oxidation state of Cr in CrO_5 is ______.

7. 0.01 mol of FeS_n (iron (II) sulphide) required 0.06 mole of AO_4^{3-} for complete oxidation. The species formed are FeO, SO_2 and A^{2+}. The value of n is ______.

8. 1575 g of oxalic acid $(COOH)_2{\cdot}xH_2O$ are dissolved in water and the volume made upto 250 mL. On titration, 16.68 mL of this solution requires 25 mL of N/15 NaOH solution for complete neutralization. The value of x is ______.

9. The equivalent weight of a metal carbonate 0.84 g of which reacts exactly with 40 mL of N/2 H_2SO_4 is ______.

10. 5 g of K_2SO_4 were dissolved in 250 mL of solution. The volume of this solution that should be used so that 1.2 g of $BaSO_4$ may be precipitated from $BaCl_2$ is ______. (Given that molar mass of $K_2SO_4 = 174\ g\ mol^{-1}$ and $BaSO_4 = 233\ g\ mol^{-1}$.)

Matrix–Match Type

1. Match the compound with the average oxidation state of Fe.

Column I	Column II
(A) $Fe_4[Fe(CN)_6]_3$	(p) 12/5
(B) $[Fe(NO)(H_2O)_5]SO_4$	(q) 2
(C) $Fe_3[Fe(CN)_6]_2$	(r) 18/7
(D) $Na_2[Fe(CN)_5NO]$	(s) 1

2. Match the reaction with its type.

Column I	Column II
(A) $V_2O_5 + 5Ca \rightarrow 2V + 5CaO$	(p) Non-metal displacement reaction
(B) $2NaH \rightarrow 2Na + H_2$	(q) Disproportionation reaction
(C) $P_4 + 3OH^- + 3H_2O \rightarrow PH_3 + 3H_2PO_2$	(r) Decomposition reaction
(D) $Ca + 2H_2O \rightarrow Ca(OH)_2 + H_2$	(s) Redox reaction

3. Match the characteristic properties with the elements.

Column I	Column II
(A) Metal which reacts with dilute acids to give H_2 gas.	(p) Zinc
(B) Metal whose container can be used to store conc. HNO_3.	(q) Silver
(C) Metal which is used as an electrode in Daniell cell.	(r) Aluminium
(D) Metal which does not react with dilute acids to give H_2 gas.	(s) Copper

(Continued)

4. Match the bold atoms in compounds with their oxidation numbers.

Column I	Column II
(A) $\mathbf{H}_2O_2$	(p) −1
(B) $\mathbf{Mn}SO_4$	(q) +3
(C) $\mathbf{Al}Cl_3$	(r) +2
(D) $\mathbf{S_2Cl_2}$	(s) +6

5. Match the reactions with equivalent weights of their oxidizing/reducing agents.

Column I	Column II
(A) $NH_3 \rightarrow \overset{-}{N}O_3$	(p) M/3
(B) $FeC_2O_4 \rightarrow Fe^{3+} + 2CO_3^{2-}$	(q) M/6
(C) $H_2SO_5 \rightarrow S_8$	(r) M/8
(D) $K\overset{+7}{Mn}O_4 \rightarrow Mn^{2+}$	(s) M/5

ANSWERS

Review Questions

1. 0, −1, +1, +3, +5, +7

2. Yes

5. H_2O_2 has been disproportionated.

6. $KClO_3$ is reduced and HNO_2 is oxidized. $KClO_3$ is the oxidizing agent and HNO_2 is the reducing agent.

10. N: +5, −3; S: +6, −2; Cl: +7, −1

11. **(a)** +6, **(b)** +6; **(c)** +5

14. $4OCl^- + S_2O_3^{2-} + H_2O \rightarrow 4Cl^- + 2SO_4^{2-} + 2H^+$

15. **(a)** No reaction; **(b)** $2Cr(s) + 3Pb^{2+}(aq) \rightarrow 2Cr^{3+}(aq) + 3Pb(s)$; **(c)** $2Ag^+(aq) + Fe(s) \rightarrow 2Ag(s) + Fe^{2+}(aq)$; **(d)** $3Ag(s) + Au^{3+}(aq) \rightarrow Au(s) + 3Ag^+(aq)$.

17. Cu < Pb < Fe < Al

18. +2

24. $Cl_2(s) + SO_2(aq) + 2H_2O(l) \rightarrow 2Cl^-(aq) + SO_4^{2-}(aq) + 4H^+(aq)$

27. 10 H^+ ions

34. **(a)** +7; **(b)** +5; **(c)** −1; **(d)** +7

35.

	(a)	(b)	(c)	(d)	(e)
Oxidized	CN^-	C_2H_5OH	I^-	$S_2O_3^{2-}$	C
Reduced	OCl^-	O_3	O_3	Cl_2	ZnO

36. 109% H_2SO_4 means strength of oleum in terms of sulphuric acid potential and 9 g of free SO_3 in 100 g oleum.

Numerical Problems

1. 26.1%
2. % of $H_2C_2O_4 \cdot 2H_2O = 26.25\%$; % of $KHC_2O_4 \cdot H_2O = 60.75\%$
3. **(a)** $IO_3^- + 3SO_3^{2-} \rightarrow I^- + 3SO_4^{2-}$; **(b)** 9.55 g Na_2SO_3
4. 51.7% S
5. 52.63 mL
6. 336.9 mL
7. $n = 2$
8. 29.4 cm^3
9. 5:1
10. 0.6 mol
11. 83.75%
12. 80.85%
13. 0.1 M
14. 100 mL
15. 5×10^{-3}M
16. 1.2044×10^{21}
17. 14 tablets
18. **(a)** 85% **(b)** 124 mL
19. **(a)** 3.82 g; **(b)** 1.847 g
20. %age of $CaCO_3 = 69$ and % age of $MgCO_3 = 31\%$
21. 14.09%

Additional Objective Questions

Single Correct Choice Type

1. (D)
2. (B)
3. (D)
4. (C)
5. (C)
6. (B)
7. (A)
8. (D)
9. (D)
10. (A)
11. (C)
12. (A)
13. (B)
14. (A)
15. (C)
16. (A)
17. (D)
18. (C)
19. (B)
20. (C)
21. (A)
22. (D)
23. (C)
24. (C)
25. (A)
26. (A)
27. (D)
28. (A)
29. (D)
30. (B)
31. (C)
32. (C)
33. (C)
34. (D)
35. (D)
36. (C)
37. (D)
38. (B)
39. (C)
40. (B)
41. (C)
42. (A)
43. (D)
44. (C)
45. (C)
46. (B)
47. (D)
48. (B)
49. (D)
50. (D)
51. (D)
52. (D)
53. (A)
54. (B)

Multiple Correct Choice Type

1. (B, C, D)
2. (A, B, C)
3. (B, C, D)
4. (B, C, D)
5. (B, C)
6. (B, C, D)
7. (A, C)
8. (B, C, D)
9. (A, C, D)
10. (A, B, C)
11. (A, D)
12. (C, D)
13. (A, B, C)
14. (B, D)
15. (A, B, C)
16. (A, C, D)
17. (A, B, C, D)
18. (A, B, D)
19. (A, B, C)
20. (A, B, C)

Assertion–Reasoning Type

1. (D)
2. (A)
3. (A)
4. (D)
5. (A)
6. (D)
7. (C)
8. (A)
9. (A)
10. (C)
11. (B)
12. (C)
13. (B)
14. (A)
15. (B)

Comprehension Type

1. (B)
2. (C)
3. (D)
4. (D)
5. (B)
6. (C)
7. (D)
8. (B)
9. (C)
10. (A)

11. (D)
12. (B)
13. (D)
14. (D)
15. (D)
16. (C)
17. (C)
18. (C)
19. (D)
20. (B)

Integer Answer Type

1. (3)
2. (1)
3. (0)
4. (7)
5. (14)
6. (7)
7. (4)
8. (2)
9. (42)
10. (45)

Matrix–Match Type

1. A → (r); B → (s); C → (p); D → (q)
2. A → (s); B → (r, s); C → (q, s); D → (p, s)
3. A → (p, r); B → (r); C → (p, s); D → (q, s)
4. A → (r); B → (s); C → (q); D → (p, r)
5. A → (r, t); B → (p); C → (q); D → (s)

3

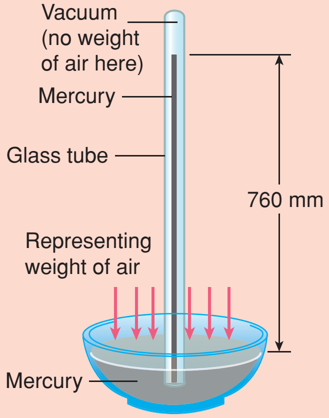
Gaseous and Liquid States

Matter is anything that occupies space and has mass. From a macroscopic view of matter associated with its bulk properties, there are three main phases: gaseous, liquid, and solid. A fourth phase, plasma exists at very high temperatures, at which ionization of atoms leads to formation of nuclei and electrons. Liquids and solids are often referred to as condensed phases because the particles in these phases are very closely packed

1. The gaseous phase of matter is generally transparent and has no definite boundaries other than those imposed by the walls of a confining vessel. Particles of a gas (atoms, molecules or ions) are well separated, have no regular arrangement and move freely at high speeds. Due to the large space in between their atoms (or molecules or ions), gases are highly compressible.
2. Particles of a liquid are close together but have no regular arrangement; they move about and slide past each other. Liquids are relatively incompressible because there is much less free space between the particles in a liquid.
3. Solids are rigid, have a definite shape and the particles are tightly packed, usually arranged in a regular pattern. The particles vibrate about their positions but do not move from place to place. Since the particles of a solid are tightly packed, they are nearly incompressible.

Since kinetic energy (K.E.) is a result of velocity of molecules, it is the highest in gases and lowest in solids. Potential energy (P.E.) is a result of intermolecular attractions. Thus, P.E. of solid state is the maximum. So at the molecular level:

1. K.E. $\gg$ |P.E.| indicates gaseous state molecule.
2. K.E. $>$ |P.E.| indicates liquid state molecule.
3. K.E. $\ll$ |P.E.| indicates solid state molecule.



Torricelli barometer

Contents

3.1 Characteristics of Gases
3.2 Pressure as Measured Property of Gas
3.3 Gas Laws
3.4 Ideal Gas Law
3.5 Payload
3.6 Variation of Pressure with Change in Density of Fluid
3.7 Faulty Barometer
3.8 Dalton's Law of Partial Pressures
3.9 Graham's Law of Effusion and Diffusion
3.10 Kinetic Theory of Gases
3.11 Molecular Collisions
3.12 Real Gases and Their Deviation from Ideal Gas Behavior
3.13 Compressibility Factor
3.14 Liquefaction of Gases
3.15 Law of Corresponding States
3.16 Heat Capacity and Specific Heats of Gases
3.17 Liquid State
3.18 Intermolecular Forces in Liquids
3.19 Characteristic Properties of Liquids: Surface Tension and Viscosity

Thus, the information required for determining the state is that what percentage of total energy is present as K.E. or P.E.

The major factor that is responsible for the varied behavior of solids, liquids and gases is the nature of the interaction that attracts one particle (atom, ion or molecule) to another and the effect of thermal energy on the movement of the particles.

A substance can exist in any of the three states depending upon the temperature and pressure under which it exists. For example, at room temperature and atmospheric pressure water exists as a liquid, it can pass into steam at same pressure but at 100°C or into solid ice at 0°C. It can exist in all three phases at 4.58 mmHg pressure and 0.0098°C temperature and this point of co-existence of three phases is known as **triple point**.

3.1 | CHARACTERISTICS OF GASES

Gases are studied before liquids and solids because of two reasons. First, the behavior of gases is easier to describe because most of the properties of gases do not depend on the identity of the gas. We can, therefore, develop a relatively simple model known as the **kinetic molecular theory** that explains most of the behavior of gases.

> **Note:** As a general rule, elements and compounds that consist of relatively light, covalent molecules are most likely to be gases at room temperature.

The most common gas familiar to people is air (roughly 21% O_2 and 79% N_2 with traces of several other gases). Some common properties of gases are listed as follows.

1. **Gases are highly compressible:** The nature of the gaseous state allows us to press a volume of gas into a smaller volume. Liquids and solids are not like that. They are essentially incompressible.
2. **Gases have low densities:** The density of a typical liquid or solid is around 2 g mL^{-1}. The density of a typical gas is around 2 g L^{-1}. This means that the density of a solid or liquid is roughly 1000 times greater than that of a gas.
3. **Gases do not have any fixed volume and shape:** Any gas will expand to fill whatever volume is available to it, even if it has to mix with other gases to do so. Liquids and solids, however, retain a constant volume when transferred from one container to another. A solid, such as an ice cube, also keeps its shape, but a liquid such as soda conforms to the shape of whatever bottle or vessel we put it in.

   Besides, the same quantity of a substance occupies a much greater volume as a gas than it does as a liquid or a solid. For example, 1 mol of water (18.02 g) has a volume of 18 mL at 4°C. This same amount of liquid water would occupy about 22,400 mL in the gaseous state. When kernels of popcorn are heated in oil, the liquids inside the kernel turn into gases. The pressure that builds up inside the kernel is enormous and eventually causes the kernel to explode. The popcorn "pops" because of the enormous difference between the volume of the liquids inside the kernel and the volume of the gases these liquids produce when they boil.
4. **Gas fills a container, uniformly exerting equal pressure in all directions:** When we blow air into a round balloon, the balloon becomes spherical and uniform. The air in the balloon obviously pushes out equally in all directions. If we were to fill the balloon with water instead (for scientific reasons only, of course), we would notice that the balloon sags. The water accumulates at the bottom of the balloon. The pressure of a gas depends on *the amount of gas*. The *more air* you pump into a tyre, the greater the pressure. The pressure of a gas rises when its temperature is increased. A sealed can, if made too hot, is in danger of exploding from the increased pressure.
5. **Gases mix thoroughly:** The gases mix thoroughly and rapidly with the surrounding air. This is a property of gases that is unique to their state. In contrast, some liquids do not mix at all (e.g., oil and water). If they do mix (e.g., water and alcohol), the mixing process occurs quite slowly.

The characteristics of gases can be described in terms of the following four parameters that can be determined experimentally:

1. **Mass or amount of gas:** The mass of gas is determined by usual weight determination methods and expressed in gram or kilograms. It can be expressed in terms of number of moles as:

$$\text{Moles } (n) = \frac{\text{Mass in grams } (m)}{\text{Molecular mass } (M)}$$

2. **Temperature:** It can be measured using a thermometer and expressed in °C or Celsius degree. The SI unit of temperature is kelvin (K) or absolute degree which is related to centigrade degree as:

$$\text{K} = {}^\circ\text{C} + 273.15$$

However for calculation purpose, we use K = °C + 273.

3. **Volume:** Since gases occupy the entire volume of the container in which they are contained, the volume of the gas is same as the volume of the container. It is expressed in liters, milliliters or cubic meter, cubic centimeter. The units are related as:

$$1\,\text{dm}^3 = 10^3\,\text{cm}^3 = 1\,\text{L} = 10^{-3}\,\text{m}^3 = 10^3\,\text{mL}$$

The volume occupied by one mole of gas at standard conditions of temperature and pressure (NTP) is called standard molar volume.

4. **Pressure:** It is the force per unit area, calculated by dividing the force by the area over which the force acts.

$$\text{Pressure} = \frac{\text{Force}}{\text{Area}}$$

For gases, it is the measure of the force exerted per unit area of the wall of the container. It is discussed in detail in the next section.

3.2 | PRESSURE AS MEASURED PROPERTY OF GAS

Earth's gravity pulls on the air mass of the atmosphere, causing it to cover the earth's surface like an invisible blanket. The molecules in the air collide with every object the air contacts, and by doing so, produce a pressure we call the *atmospheric pressure*.

To measure atmospheric pressure we use a device called a **barometer**. The simplest type is the *Torricelli barometer* (Fig. 3.1), which consists of a glass tube sealed at one end, 80 cm or more in length. To set up the apparatus, the tube is filled with mercury, capped, inverted, and then its capped end is immersed in a dish of mercury. When the cap is removed, some mercury runs out, but not all. Atmospheric pressure, pushing on the surface of the mercury in the dish, holds most of the mercury in the tube. Opposing the atmosphere is the downward pressure caused by the weight of the mercury still inside the tube. When the two pressures become equal, no more mercury can run out, but a space inside the tube above the mercury level has been created having essentially no atmosphere; it's a *vacuum*. The Torricelli barometer is also called a mercury barometer. The height of the mercury column inside the tube is directly proportional to the atmospheric pressure. In the United States, weather reports often give the height of the mercury column in inches.

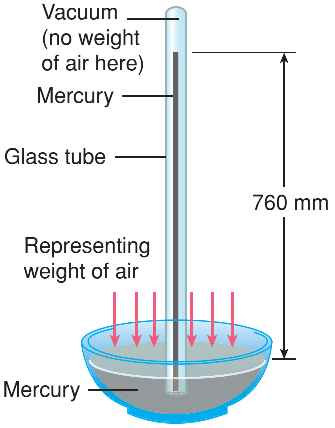


Figure 3.1 Torricelli barometer.

The height of the mercury column, measured from the surface of the mercury in the dish, is directly proportional to atmospheric pressure.

At sea level, the height of the mercury column in a barometer fluctuates around a value of 760 mm. Some days it is a little higher, some a little lower, depending on the weather. The average pressure at sea level has long been used by scientists as a standard unit of pressure. The **standard atmosphere (atm)** was originally defined as the pressure needed to support a column of mercury 760 mm high measured at 0°C. Pressure due to a fluid (gas or liquid) column can be determined as shown in Fig. 3.2.

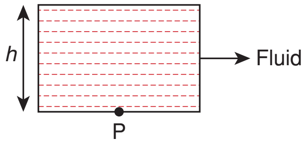


Figure 3.2 Pressure due to a fluid column.

Let the height of the fluid in the column be h and its density be ρ. If A is the area of the container, then pressure p at a point P is given by

$$\text{Pressure} = \frac{\text{Force}}{\text{Area}} = \frac{\text{Mass} \times g}{A}$$

$$p = \frac{(\rho \times hA) \times g}{A} = \rho g h$$

Units of Pressure

In the S.I., the unit of pressure is the **pascal**, symbolized **Pa**. In S.I. units, the pascal is the ratio of force in *newtons* (N, the S.I. unit of force) to area in meters squared,

$$1\ \text{Pa} = \frac{1\ \text{N}}{1\text{m}^2} = 1\ \text{N}\,\text{m}^{-2}$$

Note: 1 Pa is approximately the pressure exerted by the weight of a lemon spread over an area of 1 m^2.

To bring the standard atmosphere unit in line with other S.I. units, it has been redefined in terms of the pascal as follows.

$$1\text{atm} = 101{,}325\ \text{Pa (exactly)}$$

A unit of pressure related to the pascal is the **bar**, which is defined as 100 kPa. Consequently, one bar is slightly smaller than one standard atmosphere (1 bar = 0.9869 atm).

For ordinary laboratory work, the pascal (or kilopascal) is not a conveniently measured unit. Usually we use a unit of pressure called the **torr** (named after Torricelli). The torr is defined as 1/760th of 1 atm.

$$1\ \text{torr} = \frac{1}{760}\ \text{atm}$$

$$1\ \text{atm} = 760\ \text{torr (exactly)}$$

The torr is very close to the pressure that is able to support a column of mercury 1 mm high. In fact, the *millimeter of mercury* (abbreviated mm Hg) is often itself used as a pressure unit. Except when the most exacting measurements are being made, it is safe to use the relationship

$$1\ \text{torr} = 1\ \text{mm Hg}$$

3.3 | GAS LAWS

The four variables affecting the properties of a gas are pressure, volume, temperature and the amount of gas. In this section, we study situations in which the amount of gas (measured by either grams or moles) remains constant and observe how gas samples respond to changes in pressure, volume and temperature.

Boyle's Law

This relationship between pressure and volume is now called **Boyle's law** or the **pressure–volume law**. A graph of typical data collected in his experiments is shown in Fig. 3.3(a) and demonstrates that the volume of a given amount of gas (n) held at constant temperature varies inversely with the applied pressure. Mathematically, this can be expressed as

$$p \propto \frac{1}{V} \quad \text{(when temperature and amount of gas are constant)} \qquad (3.1)$$

where V is the volume and p is the pressure.

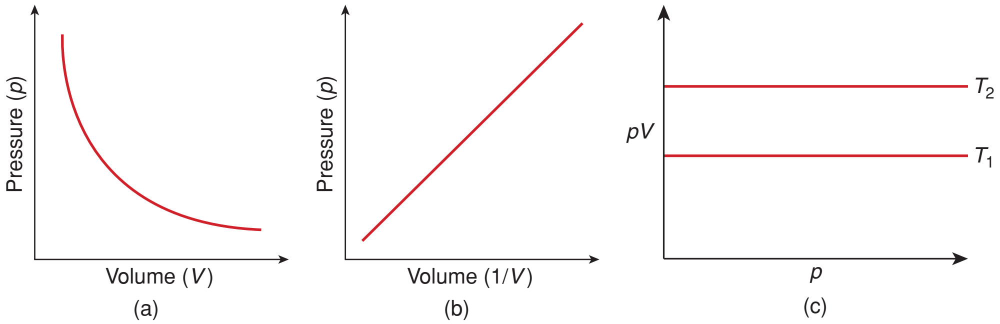


Figure 3.3 (a) Graph of p vs. V for a gas at constant temperature. (b) Graph of p vs. $1/V$ for a gas at constant temperature. (c) Graph of p vs. pV at temperature T_1 and T_2 ($T_2 > T_1$).

$$p = k_1 \frac{1}{V} \tag{3.2}$$

where k_1 a proportionality constant which depends on the temperature and amount of gas and the units of p and V. Rearranging Eq. (3.2) gives

$$pV = k_1 \tag{3.3}$$

Thus, for a fixed value of k_1, pV is constant.

Now, let us see what happens when a fixed amount of gas undergoes expansion at constant temperature. Suppose we put an ideal gas in a piston–cylinder arrangement and allow the gas to expand from an initial volume V_i to a final volume V_f while keeping the temperature T of the gas constant. Such a process, at constant temperature, is called an **isothermal expansion**.

On a p–V plot, an **isotherm** is a curve that connects points that have the same temperature. Thus, it is a graph of pressure vs. volume for a gas whose temperature T is held constant. Figure 3.4(a) shows three isotherms, each corresponding to a different (constant) value of T. Superimposed on the middle isotherm is the path followed by a gas during an isothermal expansion from state i to state f at a constant temperature of 310 K.

Note that the product of the pressure times the volume is the same number in each case as shown in Fig. 3.4(b). Substantiating Boyle's law, Eq. (3.3) can be modified as

$$p_1V_1 = p_2V_2 = k$$

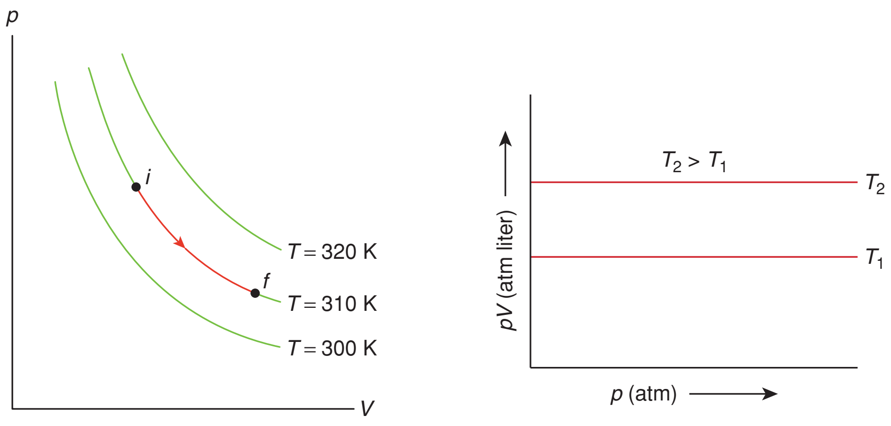
or

$$\frac{p_1}{p_2} = \frac{V_2}{V_1} \tag{3.4}$$

Equation (3.4) shows that since gases are highly compressible, so the volume proportionately decreases when the pressure increases. This also indicates that with an increase in pressure, the density of the gas increases. The density d, of a gas is its mass per unit volume, which is generally expressed in grams per liter. Substituting the value of V from Boyle's law equation, we get

$$\rho = \frac{m}{V} = \left(\frac{m}{k_1}\right)p = k'p \tag{3.5}$$

The equation confirms that when the temperature and amount of the gas are constant, the pressure is directly proportional to the density of the gas. This relationship is essentially the same for all gases at temperatures and pressures usually found in the laboratory. However, at high pressures, some deviation from Boyle's law can be seen and straight line is not obtained in the graph.



(a)

(b)

Figure 3.4 (a) Three isotherms on a p–V diagram (b) Graph of p vs. pV at temperature T_1 and T_2 ($T_2 > T_1$).

Note: The molecular explanation of the law is based on the fact that the pressure exerted by a gas arises from the impact of its particles on the walls of the vessel. If the volume is halved, the density of particles is doubled, and so twice as many particles strike the walls in a given period of time. The average force exerted by the gas is therefore doubled, and so, is the pressure it exerts.

Solved Example 3-1

What will be the pressure of the gaseous mixture when 0.5 L of H_2 at 0.8 bar and 2.0 L of dioxygen at 0.7 bar are introduced in a 1 L vessel at 27°C?

Solution

For H_2, $p_1V_1 = p_2V_2 \Rightarrow 0.8\times 0.5 = p_{H_2}\times 1 \Rightarrow p_{H_2} = 0.4$ bar

For O_2, $p_1V_1 = p_2V_2 \Rightarrow 0.7\times 2 = p_{O_2}\times 1 \Rightarrow p_{O_2} = 1.4$ bar

Therefore, $p_{\text{total}} = p_{H_2} + p_{O_2} = 0.4 + 1.4 = 1.8$ bar

Solved Example 3-2

A gas is present at a pressure of 2 atm. What should be the increase in pressure so that the volume of the gas can be decreased to 1/4th of the initial value if the temperature is maintained constant.

Solution

We know that pV = constant for a given mass of gas at constant pressure. So, $p_1V_1 = p_2V_2$. Substituting given values $p_1 = 2$ atm, $V_2 = V_1/4$, we get

$$2\times V_1 = p_2\times\frac{V_1}{4} \Rightarrow p_2 = 8 \text{ atm}$$

Therefore, the total increase in pressure is $8 - 2 = 6$ atm.

Solved Example 3-3

Two glass bulbs A and B at same temperature are connected by a very small tube having a stop cock. Bulb A has a volume of 100 cm^3 and contained the gas while bulb B was empty. On opening the stop cock, the pressure fell down to 20%. What is the volume of the bulb B?

Solution

Given that $V_1 = 100\ cm^3$, $p_1 = 100$ atm and $p_2 = 20$ atm. Thus, V_2 can be found as

$$V_2 = \frac{p_1V_1}{p_2} = \frac{100\times 100}{20} = 500\ \text{cm}^3$$

Thus, volume of B = $500 - 100 = 400\ cm^3$

Solved Example 3-4

Consider the composite system, which is held at 300 K, shown in Fig. 3.5. Assuming ideal gas behavior, calculate the total pressure if the barriers separating the compartments are removed. Assume that the volume of the barriers is negligible. (Given: $R = 0.082$ atm L^{-1} $mol^{-1}K^{-1}$.)

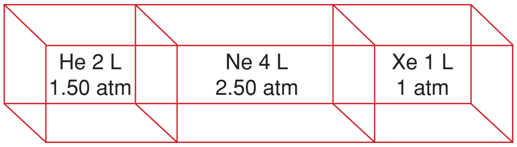


Figure 3.5

Solution

$$p_1V_1 + p_2V_2 + p_3V_3 = p_4V_4$$

$$2\times 1.5 + 4\times 2.5 + 1\times 1 = 7\times p_T \Rightarrow p_T = 2 \text{ atm}$$

Charles' Law

The quantitative effect of temperature on the volume of a sample of gas at constant pressure was first advanced by a French scientist, Jacques Charles, in 1787. Charles showed that any gas expands by a definite fraction as the temperature rises. He found that the volume increases by a fraction of 1/273.15 for each 1°C rise in the temperature (Fig. 3.6).

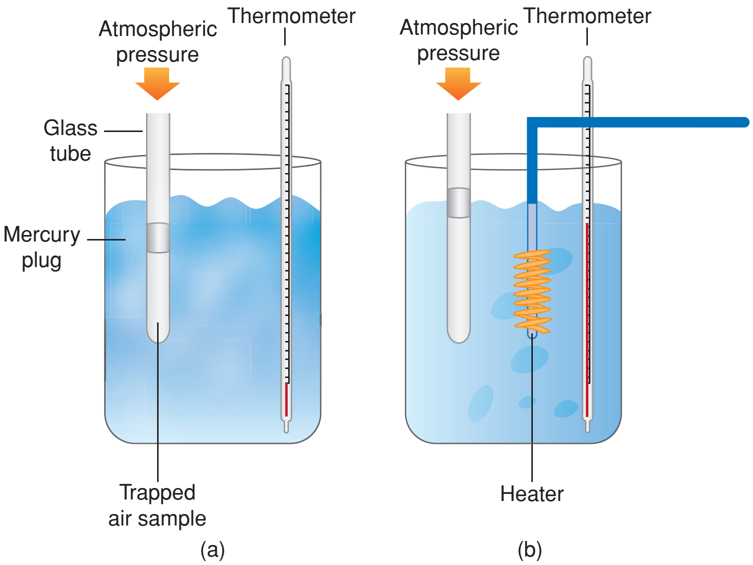


Figure 3.6 The relationship between temperature and volume: (a) An ice water bath at 0°C. (b) A boiling water bath at 100°C.

Next, he studied what happens to the volume of a sample of gas when the temperature is varied, keeping the pressure constant. When the volume of the gas is plotted against the temperature in degrees Celsius using the data from experiments, graph shown in Fig. 3.7(a) is obtained. Each line is called an **isobar** and shows how the gas volume changes with temperature for a different size sample of the same gas. Since all gases eventually become liquids if cooled sufficiently, the solid portions of the lines correspond to temperatures at which measurements are possible; at lower temperatures, the gas liquefies. However, if the lines are extrapolated (reasonably extended) back to a point where the volume of the gas would become zero if it did not condense, it was observed that all the lines meet at the same temperature, –273.15°C. Especially significant is the fact that this exact same behavior is exhibited by all gases. This point represents the nature's coldest temperature, and it was called **absolute zero**.

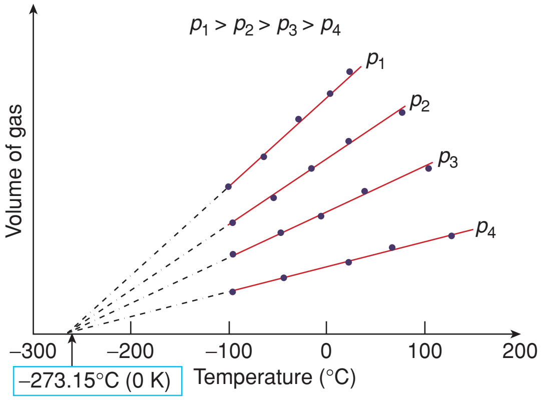


Figure 3.7 Charles' law plots V vs. T (Celsius) at different constant pressures.

At absolute zero temperature, translational motion (motion from point to point) ceases. This absolute zero corresponds to the zero point on the **Kelvin temperature scale** or **Absolute temperature scale**. To obtain a Kelvin temperature, we add 273.15°C to the Celsius temperature.

$$T_{\text{Kelvin}} = 273.15 + T_{\text{Celsius}} \tag{3.6}$$

Similarly, 0°C is given by $T_0 = 273.15$ and is equal to 273.15 K on the Kelvin temperature scale, also known as **thermodynamic scale**. For most purposes, we will need only three significant figures, so we can use 273 instead of 273.15.

If V_0 and V_T are the volumes at temperatures 0°C and T°C, then

$$V_T = V_0\left(1+\frac{T}{273.15}\right)$$

The straight lines in Fig. 3.7 suggest that at constant pressure, the volume of a gas is directly proportional to its temperature, provided the temperature is expressed in kelvins. This became known as **Charles' law** (or the **temperature–volume law**) and is expressed mathematically as

$$V \propto T \tag{3.7}$$

The relationship between volume and temperature noted by Charles can now be restated in terms of the Kelvin scale. Charles's law **states that the volume of a gas is directly proportional to the Kelvin temperature (*T*) at constant pressure**. (From this point on, T will represent the Kelvin temperature exclusively.) This can be expressed mathematically as a proportion or as equality, with k_2 serving as the symbol for the constant of proportionality.

$$V = k_2T \quad \text{or} \quad \frac{V}{T} = k_2 \tag{3.8}$$

The value of k_2 depends on the amount and pressure of the gas and the unit of volume. For a quantity of gas at two temperatures at the same pressure, we have

$$\frac{V_2}{T_2} = \frac{V_1}{T_1} \tag{3.9}$$

This equation can be used to calculate how the volume of gas changes when the temperature changes. For example, if V_2 is a new volume that we are to find at a given new temperature T_2, the equation becomes

$$V_2 = V_1 \times \frac{T_2}{T_1} \tag{3.10}$$

Charles's law is obeyed by all gases at high temperatures and very low pressures.

Solved Example 3-5

Two vessels connected by a valve of negligible volume. One container (I) has 2.8 g of N_2 at temperature T_1(K). The other container (II) is completely evacuated. The container (I) is heated to T_2(K), while container (II) is maintained at $T_2/3$(K). Volume of vessel (I) is half of that of vessel (II). If the valve is opened, then what is the weight ratio of N in both vessels($w_{\text{I}}/w_{\text{II}}$)?

Solution

From the expression, we have

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

or

$$\frac{1/2V_1}{T_2} = \frac{V_2}{T_2} \Rightarrow \frac{V_1}{2T_2} = \frac{3V_2}{T_2} = \frac{V_1T_2}{6T_2V_2} = \frac{1}{6}$$

Solved Example 3-6

For a closed (not rigid) container containing $n = 10$ mol of an ideal gas fitted with movable, frictionless, weightless piston operating such that pressure of the gas remains constant at 0.821 atm. Draw the graph that represents correct variation of log V vs. log T, where V is in liter and T in kelvin?

Solution

From Charles law, we have $V \propto T$. Taking log on both sides, we get

$$\log V = \log T + \log \text{constant } (c) \Rightarrow \log V = \log T + c$$

Comparing with $y = mx + c$, we get $m = 1$ and $c = 1$. So, $\theta = 45°$.

Therefore, $$\frac{w_1}{w_2} = \frac{1}{6}$$

The graph is shown in Fig. 3.8.

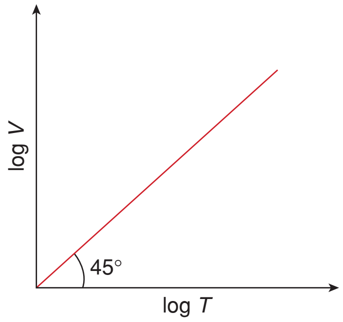


Figure 3.8

Solved Example 3-7

A student forgot to add the reaction mixture to the round bottomed flask at 27°C but put it on the flame. After a lapse of time, he realized his mistake. Using a pyrometer, he found that the temperature of the flask was 477°C. What fraction of the air would have been expelled out?

Solution

Let the volume of the air in the flask at 27°C (300 K) be V_1 and that of the same amount of the gas at 477°C (750 K) be V_2. According to the Charle's law, we get

$$\frac{V_2}{V_1} = \frac{T_2}{T_1} \tag{1}$$

Volume of the gas expelled out $= V_2 - V_1$. Then, fraction of the gas expelled out is

$$\frac{V_2 - V_1}{V_2} = 1 - \frac{V_1}{V_2} \tag{2}$$

From Charles law one can write, $\frac{V_2}{V_1} = \frac{T_2}{T_1}$. Substituting this value in Eq. (2), we get

$$\text{Fraction of the air expelled} = 1 - \frac{T_1}{T_2} = \frac{T_2 - T_1}{T_2} = \frac{750 - 300}{750} = \frac{450}{750} = \frac{3}{5} = 0.6$$

Thus, three-fifth (0.6) of the gas is expelled out.

Gay–Lussac's Law

When a confined quantity of gas is heated, the pressure increases. The relationship between temperature and pressure was proposed in 1802 by Joseph Louis Gay–Lussac. This French scientist studied how the pressure and temperature of a fixed amount of gas at constant volume are related. The relationship that he established, called **Gay–Lussac's law** or the **pressure–temperature law**, **states that the pressure of a fixed amount of gas held at constant volume is directly proportional to the temperature**. Thus,

$$p \propto T \quad \text{(when volume and amount of gas is kept constant)} \tag{3.11}$$

Using still another constant of proportionality k_3, Gay–Lussac's law becomes

$$p = k_3 T \quad \text{or} \quad k_3 = \frac{p}{T} \tag{3.12}$$

Boyle's and Charles' laws can be used to derive Eq. (3.12). The plot of pressure vs. temperature (in K) is shown in Fig. 3.9. Each line in this graph is called an **isochore**. At constant volume for a fixed amount of gas, the pressure is proportional to the absolute temperature.

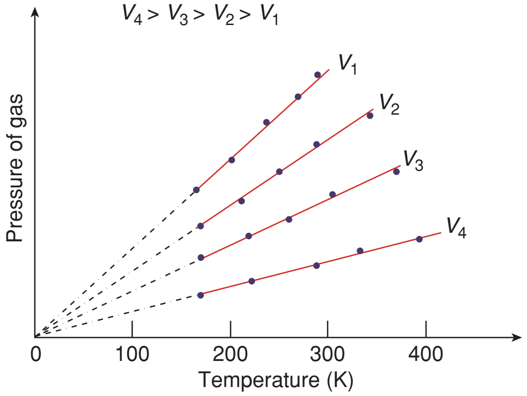


Figure 3.9 Plot of pressure vs. temperature for different constant volumes of gas.

Note: Deodorant cans carry a warning: *Do Not Store Near Heat*. This is because the spray is stored as a gas in the can of fixed volume. On heating, since the volume of the can is fixed, the pressure will increase. Eventually, the seal on the can breaks off and an explosion occurs.

Avogadro's Law

If the volumes of the reacting gases, as well as the volumes of gaseous products, are measured under the same conditions of temperature and pressure, the volumes are in simple whole number ratios. For example, hydrogen gas reacts with chlorine gas to give gaseous hydrogen chloride. Beneath the names in the following equation are the relative volumes with which these gases interact (at the same T and p).

$$\underset{\text{1 volume}}{\text{Hydrogen}} + \underset{\text{1 volume}}{\text{Chlorine}} \rightarrow \underset{\text{2 volumes}}{\text{Hydrogen chloride}}$$

The observation that gases react in whole-number volume ratios led Amedeo Avogadro (1776–1856), an Italian scientist, to conclude that, at the same T and p, equal volumes of gases must have identical numbers of molecules. We know now that "equal numbers of molecules" is the same as "equal numbers of **moles**," so Avogadro's insight, now called **Avogadro's principle**, is expressed as follows: **When measured at the same temperature and pressure, equal volumes of gases contain equal numbers of moles**. A corollary to Avogadro's principle is that **the volume of a gas is directly proportional to its number of moles, *n***.

$$V \propto n \quad \text{(at constant } T \text{ and } P) \tag{3.13}$$

Therefore,

$$V = k_4 n \tag{3.14}$$

It has already been discussed in Chapter 1 that the number of molecules in one mole of a gas is 6.023×10^{23} which is known as **Avogadro's constant**. Rearranging Eq. (3.14) in terms of density, we have

$$V = k_4 \frac{m}{M} \Rightarrow M = k_4 \frac{m}{V}$$

or $$M = k_4\rho \tag{3.15}$$

where ρ is the density of gas which is directly proportional to the molar mass M.

Note: Earlier, the term **Avogadro's number**, which is closely related to the Avogadro constant was used. After revisions in the base set of S.I. units, the term Avogadro's constant came into existence. It was defined as the number of molecules in 1 g molecule of hydrogen. It is a dimensionless quantity and has the numerical value of the Avogadro constant given in base units.

Avogadro's principle implies that the volume occupied by one mole of *any* gas – its *molar volume* – must be identical for all gases under the same conditions of pressure and temperature. To compare the molar volumes of different gases, scientists agreed to use 1 bar (10^5 Pa) and 273.15 K (0°C) as the **standard conditions of temperature and pressure** (**STP**). These values of temperature and pressure are approximately equal to the freezing temperature of water and atmospheric pressure at sea level. If we measure the molar volumes for a variety of gases at STP, we find that the values fluctuate somewhat because the gases are not "ideal". Some typical values are shown in Table 3.1 and if we were to examine the data for many gases, we would find an average of around 22.4 L per mole. This value is taken to be the molar volume of an *ideal gas* at STP and is now called the **standard molar volume** of a gas.

Table 3.1 Molar volumes of some gases

Gas	He	Ar	H_2	N_2	O_2	CO_2	NH_3	Ideal gas
Molar volume (L)	22.398	22.401	22.410	22.413	22.414	22.414	22.09	22.41

Solved Example 3-8

How many liters of hydrogen, measured at STP, are needed to combine exactly with 1.50 L of nitrogen, also measured at STP, to form ammonia?

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

Solution

The volume of hydrogen is given in liters, so we need to express the volume equivalency in those units as well.

$$3\text{L of } H_2 \Leftrightarrow 1\text{L of } N_2$$

We then multiply the given amount, 1.50 L of N_2, by a conversion factor made from the equivalency above:

$$\text{Volume of } H_2 = 1.50 \text{ L of } N_2 \times \frac{3 \text{ L of } H_2}{1 \text{ L of } N_2} = 4.50 \text{ L of } H_2$$

Solved Example 3-9

How many liters of air (air is 21% oxygen) are required for the combustion of 6.75 L of CH_4? (Assume air and CH_4 are at the same T and p.)

Solution

From the given values, we have

$$\text{Volume of } O_2 = (6.75 \text{ L } CH_4)\left(\frac{2 \text{ volume } O_2}{1 \text{ volume } CH_4}\right) = 13.50 \text{ L}$$

or $$21\% \ O_2 = \frac{13.50 \text{ L } O_2}{x \text{ L air}} \times 100\%$$

or $$\text{Volume of air} = (13.50 \text{ L } O_2)\left(\frac{100\%}{21\%}\right) = 64.3 \text{ L}$$

Solved Example 3-10

Methane burns according to the following equation:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$$

The combustion of 4.50 L of CH_4 consumes how many liters of O_2, both volumes measured at 25°C and 740 mm Hg? (Hint: Recall Avogadro's principle concerning the number of molecules in a fixed volume of gas at a given temperature and pressure.)

Solution

When gases are held at the same temperature and pressure, and dispensed in this fashion during chemical reactions, then they react in a ratio of volumes that is equal to the ratio of the coefficients (moles) in the balanced chemical equation for the given reaction. We can, therefore, directly use the stoichiometry of the balanced chemical equation to determine the combining ratio of the gas volumes:

$$\text{Volume of } O_2 = (4.50 \text{ L } CH_4)\left(\frac{2 \text{ volume } O_2}{1 \text{ volume } CH_4}\right) = 9.00 \text{ L}$$

Combined Gas Laws

In Eq. (3.11), varying the three variables p, V and T for a fixed amount of gas as follows:

Initial conditions: $p = p_1$, $V = V_1$ and $T = T_1$

Final conditions: $p = p_2$, $V = V_2$ and $T = T_2$

The equation can be written as

$$\frac{p_1V_1}{T_1} = nR \quad \text{and} \quad \frac{p_2V_2}{T_2} = nR$$

or

$$\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2} \tag{3.16}$$

Equation (3.16) is called the **combined gas law** and states that the ratio pV/T is a constant for a fixed amount of gas. Alternately, Eq. (3.16) can be derived by combining the three gas laws – Boyle's, Charles' and Gay–Lussac's laws.

$$p_1V_1 = p_2V_2 \text{ (for } T_1 = T_2) \qquad \frac{V_1}{T_1} = \frac{V_2}{T_2} \text{ (for } p_1 = p_2) \qquad \frac{p_1}{T_1} = \frac{p_2}{T_2} \text{ (for } V_1 = V_2)$$

Hence, on combining the above three equations, we arrive at the combined gas law given by Eq. (3.16).

Note that in applying this equation, T must always be in kelvins. The pressure and volume can have any units, but whatever the units are on one side of the equation, they must be the same on the other side.

Solved Example 3-11

Nitrogen monoxide, a pollutant released by automobile engines, is oxidized by molecular oxygen to give the reddish brown gas nitrogen dioxide, which gives smog its characteristic color. The equation is

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

How many milliliters of O_2 measured at 20°C and 755 mm Hg are needed to react with 180 mL of NO, measured at 45°C and 720 mm Hg?

Solution

The first step is to use the combined gas law applied to the given volume of NO, so let us set up the data as usual.

Variable	Initial	Final
p	720 mm Hg	755 mm Hg
V	180 mL	?
T	318 K (45°C + 273)	293 K (20°C + 273)

Solving the combined gas law for V_2 gives

$$V_2 = V_1 \times \left(\frac{p_1}{p_2}\right) \times \left(\frac{T_2}{T_1}\right)$$

Next we substitute values,

$$V_2 = 180\ \text{mL} \times \left(\frac{720\ \text{mm Hg}}{755\ \text{mm Hg}}\right) \times \left(\frac{293\ \text{K}}{318\ \text{K}}\right) = 158\ \text{mL of NO}$$

Now we have the volume of NO *at the same temperature and pressure as the oxygen*. This lets us use the coefficients of the equation to establish the equivalency

$$2\ \text{mL of NO} \Leftrightarrow 1\ \text{mL of } O_2$$

and apply it to find the volume of O_2 required for the reaction.

$$158\ \text{mL of NO} \times \frac{1\ \text{mL of } O_2}{2\ \text{mL of NO}} = 79.0\ \text{mL of } O_2$$

Solved Example 3-12

Butane (C_4H_{10}) is the fuel in cigarette lighters. It burns in oxygen according to the equation

$$2C_4H_{10}(g) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(g)$$

How many milliliters of O_2 at 35°C and 725 mm Hg are needed to react completely with 75.0 mL of C_4H_{10} measured at 45°C and 760 mm Hg?

Solution

Starting with the combined gas law:

$$\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$$

Rearrange the equation to find a new volume (V_2)

$$V_2 = \frac{p_1V_1T_2}{T_1p_2}$$

Calculate the new volume for the butane (C_4H_{10}) using the temperature and pressure of the oxygen (O_2)

$$V_2 = \frac{(760\ \text{torr})(75.0\ \text{mL})(308\ \text{K})}{(318\ \text{K})(725\ \text{torr})} = 76.1\ \text{mL } C_4H_{10}$$

Now calculate the number of mL of O_2 require to react with 76.1 mL C_4H_{10}

$$\text{mL } O_2 = 76.1\ \text{mL } C_4H_{10}\left(\frac{13\ \text{volume } O_2}{2\ \text{volume } C_4H_{10}}\right) = 495\ \text{mL}$$

Solved Example 3-13

A rigid vessel of volume 0.50 m^3 containing H_2 at 20.5°C and a pressure of 611×10^3 Pa is connected to a second rigid vessel of volume 0.75 m^3 containing Ar at 31.2°C at a pressure of 433×10^3 Pa. A valve separating the two vessels is opened and both are cooled to a temperature of 14.5°C. What is the final pressure in the vessels?

Solution

Given that at volume of 0.50 m^3, V_1 = 500 mL, T_1 = 20.5°C = 293.5 K, p_1 = 611 × 10^3 Pa = 6 atm. At volume 0.75 cm^3, V_2 = 750 L, T_2 = 31.2°C = 304.2 K, p_2 = 433 × 10^3 Pa = 4.27 atm.

The valve is opened and both are cooled to 14.5°C temperature, that is, T_3 = 14.5°C = 287.5 K, final pressure (p_3), V_3 = 500 + 750 = 1,250 mL

Substituting in the below expression, we get

$$\frac{p_1V_1}{T_1} + \frac{p_2V_2}{T_2} = \frac{p_3V_3}{T_3} \Rightarrow \frac{6 \times 500}{293.5} + \frac{4.27 \times 750}{304.2} = \frac{p_3 \times 1{,}250}{287.5}$$

or $$10.22 + 1{,}053 = \frac{p_3 \times 1{,}250}{287.5}$$

or $$p_3 = 4.77\ \text{atm} = 4.77 \times 101.3 \times 10^3\ \text{Pa} = 4.83 \times 10^5\ \text{Pa}$$

3.4 | IDEAL GAS LAW

So far, gases have been described in terms of four variables: pressure (p), volume (V), temperature (T), and the number of moles of gas (n). In each case, two of the variables were allowed to change while the other two were held constant. The relationships between pairs of variables can be summarized as

Boyle's law: $p \propto 1/V$ (T and n constant)

Charles' law: $V \propto T$ (p and n constant)

Avogadro's hypothesis: $V \propto n$ (p and T constant)

Based on the three relations, we have $V \propto \dfrac{nT}{p} \Rightarrow V = R\dfrac{nT}{p}$

Rearranging the equation, we get

$$pV = nRT \tag{3.17}$$

where R is a proportionality constant known as the **ideal gas constant** and T is the absolute temperature. Equation (3.17) can be rearranged and written as follows.

$$\frac{pV}{nT} = R \tag{3.18}$$

This equation is also called the **universal gas law** and R is known as **universal gas constant**. An ideal gas would obey this relationship known as **ideal gas equation** exactly over all ranges of the gas variables.

According to the **ideal gas law**, the product of pressure times volume of an ideal gas divided by the product of amount of gas times absolute temperature is a constant.

Note: Real gases do not *exactly* obey these gas laws, it is often useful to imagine a hypothetical gas and call that as an **ideal gas**, which would obey the gas laws (Boyle's and Charles' laws) exactly over all temperatures and pressures. A real gas behaves more and more like an ideal gas as its pressure decreases and its temperature increases or when its volume increases as the temperature increases. Most of the gases on which experiments are conducted can be treated as ideal gases unless we are dealing with extremely precise measurements.

Equation (3.17) tells us how the four important variables for a gas, p, V, n, and T are related. If we know the values of three, we can calculate the fourth. We can define the *state* of a given gas simply by specifying any three of the four variables so it is also called **equation of state**. If n, p and T in Eq. (3.17) are known, for example, then V *can have only one value*.

Dimension and Numerical Values of *R*

The gas equation for one mole of gas can be written as: $pV = RT$. Therefore,

$$R = \frac{pV}{nT} = \frac{\text{Pressure} \times \text{Volume}}{\text{Moles} \times \text{Temperature}} = \frac{\text{Force}}{\text{Area}} \times \frac{\text{Volume}}{\text{Moles} \times \text{Temperature}}$$

$$= \frac{\text{Force}}{\text{Area}} \times \frac{\text{Area} \times \text{Length}}{\text{Moles} \times \text{Temperature}} = \frac{\text{Work(Energy)}}{\text{Moles} \times \text{Temperature}}$$

So, the dimension of R is energy per degree per mole.

To use the ideal gas law, we have to know the value of the universal gas constant, R. To calculate it, we use the standard conditions of pressure and temperature, and we use the standard molar volume, which sets n equal to 1 mol, the number of moles of the sample. The value of R depends on the units used to express the four variables p, V, n and T. Suppose we express volume in *liters* and pressure in *atmospheres*. Then for 1 M volume at STP, $n = 1$ mol, $V = 22.710981$ L, $p = 1.0$ atm and $T = 273.15$ K. Substituting these values in Eq. (3.18), we calculate R as follows.

$$R = \frac{pV}{nT} = \frac{(1.0\text{ atm}) \times (22.4\text{ L})}{(1.0\text{ mol}) \times (273.15\text{ K})} = 0.0821\text{ L atm mol}^{-1}\text{K}^{-1}$$

To use this value of R in working problems, we have to be sure to express volumes in liters and pressures in atmospheres. And, of course, temperatures must be expressed in kelvins. More precise measurements give $R = 0.082057$ L atm mol^{-1} K^{-1}. Using Eq. (3.18), at conditions of temperature 273.15 K and 1 bar pressure, we get $R = 8.314$ J K^{-1} mol^{-1}.

Solved Example 3-14

An important chemical reaction in the manufacture of Portland cement is the high temperature decomposition of calcium carbonate to give calcium oxide and carbon dioxide. Suppose a 1.25 g sample of calcium carbonate is decomposed by heating. How many milliliters of carbon dioxide gas will be evolved if the volume is measured at 740 mm Hg and 25°C?

Solution

The formula mass of $CaCO_3$ is 100.1, so

$$\text{Moles of } CaCO_3 = 1.25 \text{ g } CaCO_3 \times \frac{1 \text{ mol } CaCO_3}{100.1 \text{ g } CaCO_3} = 1.25 \times 10^{-2} \text{ mol of } CaCO_3$$

Because 1 mol $CaCO_3 \Leftrightarrow$ 1 mol CO_2, therefore, $n = 1.25 \times 10^{-2}$ mol of CO_2.

Before we use n in the ideal gas law equation, we must convert the given pressure and temperature into the units required by R.

$$p = 740 \text{ mm Hg} \times \frac{1 \text{ atm}}{760 \text{ mm Hg}} = 0.974 \text{ atm}$$

$$\text{and} \quad T = 25 + 273 = 298 \text{ K}$$

By rearranging the ideal gas law equation we obtain

$$\begin{aligned} V &= \frac{nRT}{p} \\ &= \frac{(1.25 \times 10^{-2} \text{ mol}) \times (0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}) \times (298 \text{ K})}{0.974 \text{ atm}} \\ &= 0.314 \text{ L} = 314 \text{ mL} \end{aligned}$$

The reaction will yield 314 mL of CO_2 at the conditions specified.

Density and Molar Mass Measurement of a Gas

The molar mass of a gaseous compound can be found using experimental values of pressure, volume, temperature and sample mass. The p, V, T data allow us to calculate the number of moles using the ideal gas law. Once we know the number of moles of gas and the mass of the gas sample, the molar mass is obtained by taking the ratio of *grams to moles*.

The relation between molar mass and density can be derived as follows. This relation helps in determining the density/molar mass of a substance, if all the other terms are known. Using the ideal gas equation, $pV = nRT$, and substituting $n = m/M$ where m is the given mass and M is the molar mass, we get

$$pV = \frac{m}{M}RT$$

Rearranging, we get

$$pM = \frac{m}{V}RT \Rightarrow pM = \rho RT$$

where ρ is the density of the gas in gram per liter. Hence, knowing density of a substance, molar mass can be calculated as

$$M = \frac{\rho RT}{p} \tag{3.19}$$

The density of an ideal gas can thus be obtained using the ideal gas equation. The vapor density of the gas is different from the density and is given by:

$$\text{Vapor density} = \frac{\text{Mass of } V \text{ mL of gas (at } p, T)}{\text{Mass of } V \text{ mL of } H_2 \text{ (at } p, T)} \tag{3.20}$$

It is a ratio and has no units and is independent of pressure and temperature.

The density of the gas is the ratio of molar mass to molar volume and increases with decrease in pressure and decreases with increase in temperature.

Solved Example 3-15

As part of a rock analysis, a student added hydrochloric acid to a rock sample and observed a fizzing action, indicating a gas was being evolved. The student collected a sample of the gas in a 0.220 L gas bulb until its pressure reached 0.757 atm at a temperature of 25.0°C. The sample weighed 0.299 g. What is the molar mass of the gas? What kind of compound was the likely source of the gas?

Solution

Pressure is already in atmospheres and the volume is in liters, but we must convert degrees Celsius into kelvins. Gathering our data, we have $p = 0.757$ atm, $V = 0.220$ L, $T = 25 + 273 = 298$ K.

Next, we solve the ideal gas law ($pV = nRT$) for the number of moles, n.

$$n = \frac{pV}{RT}$$

Now we can substitute the data for p, V and T, along with the value of R. This gives

$$n = \frac{(0.757\text{ atm})\times(0.220\text{ L})}{(0.0821\text{ L atm mol}^{-1}\text{ K}^{-1})\times(298\text{ K})} = 6.81\times10^{-3}\text{ mol}$$

The molar mass is obtained from the ratio of grams to moles.

$$\text{Molar mass} = \frac{0.299\text{ g}}{6.81\times10^{-3}\text{ mol}} = 43.9\text{ g mol}^{-1}$$

We now know the measured molar mass is 43.9 g mol^{-1}, but what gas could this be? The gases given off when a substance reacts with acids might be H_2S, HCN, CO_2 or SO_2. Using atomic masses to calculate their molar masses, we get

H_2S	34 g mol^{-1}	CO_2	44 g mol^{-1}
HCN	27 g mol^{-1}	SO_2	64 g mol^{-1}

The only gas with a molar mass close to 43.9 g mol^{-1} is CO_2, and that gas would be evolved if we treat a carbonate with an acid. The rock probably contains a carbonate compound. (Limestone and marble are examples of such minerals.)

Solved Example 3-16

One procedure used to separate the isotopes of uranium to obtain material to construct a nuclear weapon employs a uranium compound with the formula UF_6. The compound boils at about 56°C, so at 100°C it is a gas. What is the density of UF_6 at 100°C if the pressure of the gas is 740 mm Hg? (Assume the gas contains the mix of uranium isotopes commonly found in nature.)

Solution

The pressure is 740 mm Hg, so to convert to atmospheres, we use the relationship between the atmosphere and mm Hg.

$$740\text{ mm Hg}\times\frac{1\text{ atm}}{760\text{ mm Hg}} = 0.974\text{ atm}$$

The temperature is 100°C, which converts to 373 K, and we said we would use $n = 1.00$ mol. To find the molar volume, we solve the ideal gas law for V.

$$V = \frac{nRT}{p}$$

Now, we substitute values

$$V = \frac{1.00\text{ mol}\times0.0821\text{ L atm mol}^{-1}\text{ K}^{-1}\times373\text{ K}}{0.974\text{ atm}} = 31.4\text{ L}$$

At these conditions of temperature and pressure, the molar volume is 31.4 L mol^{-1}. To calculate the density, we need one more piece of data, the molar mass of UF_6. Adding up the atomic masses, we get a molar mass of 352.0 g mol^{-1}. Using the relation between molar mass and density, we get

$$M = \frac{\rho RT}{p} \Rightarrow \rho = \frac{Mp}{RT} = \frac{M}{V} \quad (\text{as } V = RT/p \text{ for 1 mol})$$

Therefore, the density is

$$\rho = \frac{352.0\text{ g}}{31.4\text{ L}} = 11.2\text{ g L}^{-1}$$

Solved Example 3-17

A liquid used as a dry cleaning solvent, has an empirical formula CCl_2 and a boiling point of 121°C. When vaporized, the gaseous compound has a density of 4.93 g L^{-1} at 785 mm Hg and 150°C. What is the molar mass of the compound and what is its molecular formula?

Solution

To calculate the number of moles of gas in 1.00 L, we use the ideal gas law, making unit conversions as needed. The data are given as $T = 150 + 273 = 423$ K; $p = 785$ mm Hg × (1 atm/760 mm Hg) = 1.03 atm; $V = 1.00$ L.

Solving the ideal gas law for n and substituting values, we have

$$n = \frac{pV}{RT} = \frac{(1.03 \text{ atm}) \times (1.00 \text{ L})}{(0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}) \times (423 \text{ K})}$$
$$= 2.97 \times 10^{-2} \text{ mol}$$

Now we can calculate the molar mass by dividing the mass 4.93 g by the number of moles, 2.97×10^{-2} mol.

$$\frac{4.93 \text{ g}}{2.97 \times 10^{-2} \text{ mol}} = 166 \text{ g mol}^{-1}$$

The molar mass of the compound is thus 166 g mol^{-1}.

The empirical formula mass that we calculate from the empirical formula, CCl_2, is 82.9. We now divide the molar mass by this value to see how many times CCl_2 occurs in the molecular formula.

$$\frac{166}{82.9} = 2.00$$

To find the molecular formula, we multiply the subscripts of the empirical formula by 2.

$$\text{Molecular formula} = C_{1\times2}\, Cl_{2\times2} = C_2Cl_4$$

(This is the formula for a compound commonly called tetrachloroethylene, which is indeed used as a dry cleaning fluid.)

Solved Example 3-18

When a 158 mL lightbulb is filled with argon at a temperature of 20°C and a pressure of 3.00 mm Hg. How many grams of argon are in the lightbulb under these conditions?

Solution

To use $R = 0.0821$ L atm mol^{-1} K^{-1}, we must have V in liters, p in atmospheres, and T in kelvins. Gathering the data and making the necessary unit conversions as we go, we have

$$p = 3.00 \text{ mm Hg} \times \frac{1 \text{ atm}}{760 \text{ mm Hg}} = 3.95 \times 10^{-3} \text{ atm}$$

and $V = 158 \times 10^{-3}$ L $= 0.158$ L, $T = 20 + 273 = 293$ K. Solving the ideal gas law for n gives us

$$n = \frac{pV}{RT}$$

Substituting the proper values of p, V, R and T into this equation gives

$$n = \frac{(3.95 \times 10^{-3} \text{ atm}) \times (0.158 \text{ L})}{(0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}) \times (293 \text{ K})}$$
$$= 2.59 \times 10^{-5} \text{ mol of Ar}$$

The atomic mass of Ar is 39.95, so 1 mol Ar = 39.95 g Ar. A conversion factor made from this relationship lets us convert "mol Ar" into "g Ar".

$$2.59 \times 10^{-5} \text{ mol of Ar} \times \frac{39.95 \text{ g of Ar}}{1 \text{ mol of Ar}} = 1.04 \times 10^{-3} \text{ g of Ar}$$

Thus, the light bulb contains only about one-thousandth of a gram of argon.

Solved Example 3-19

When 3.2 g of sulphur is vaporized at 450°C and 723 mm pressure, the vapors occupy a volume of 780 mL. What is the molecular formula of sulphur vapors under these conditions? Calculate the vapor density also.

Solution

From ideal gas equation, we have $pV = nRT$, or

$$pV = \left(\frac{w}{M}\right) RT \Rightarrow \frac{723}{760} \times \frac{780}{1000} = \frac{3.2}{M} \times 0.082 \times 723$$
$$\Rightarrow M = 255.67 \text{ g mol}^{-1}$$

The number of atoms of sulphur in one molecule $= M/32 = 255.67/32 = 8$. So, the molecular formula of sulphur $= S_8$. Now, vapor density is

$$\text{Vapor density} = \frac{M}{2} = \frac{255.67}{2} = 127.84$$

Illustrations Based on Mercury Column

Consider a test tube open at one end and closed at other that encloses an air column 7 cm long by a 10 cm long Hg column as shown in Fig. 3.10(a). Let the area of cross-section be A and pressure due to air-column be p. The forces acting on the Hg column are as illustrated in Fig. 3.10 (b). Hg is in equilibrium and both the forces will be in equilibrium. So,

$$pA = 76\,A \Rightarrow p = 76 \text{ cm of Hg}$$

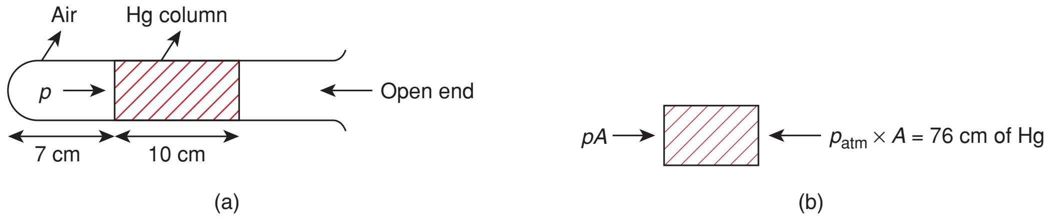


Figure 3.10 (a) Mercury and air column. (b) Forces acting on mercury column.

We can determine the length of air column for the following conditions:

(a) When the test tube is held vertically with open end upwards (Fig. 3.11). The forces acting on the Hg column are depicted in Fig. 3.11(b).

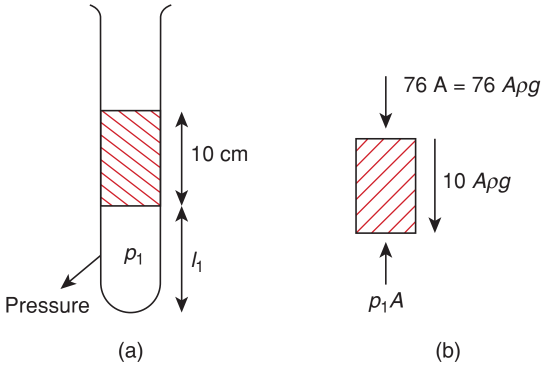


Figure 3.11 (a) Test tube held vertically with open end upwards. (b) Forces acting on Hg column.

Since Hg is a liquid, its volume will not change. Let ρ be the density of Hg. Then,

$$76A\rho g + 10A\rho g = p_1A$$

$$p_1 = 86\rho g \text{ or } 86 \text{ cm of Hg}$$

For the air which is enclosed, the number of moles and temperature is constant. Therefore, from Boyle's law

$$p_1V_1 = p_2V_2$$
$$76 \times 7A = 86 \times l_1 \times A$$
$$l_1 = 6.18 \text{ cm}$$

(b) When the test tube is held vertically with open end downwards as shown in Fig. 3.12(a). Then forces acting on the Hg column are depicted in Fig. 3.12(b).

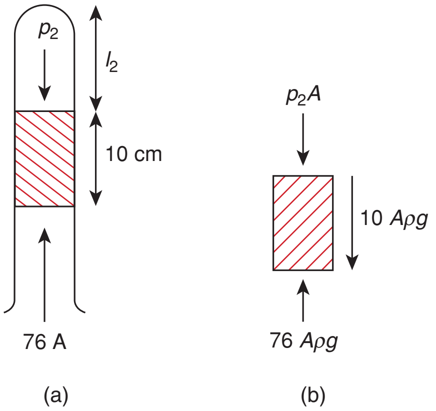


Figure 3.12 (a) Test tube held vertically with open end downwards. (b) Forces acting on Hg column.

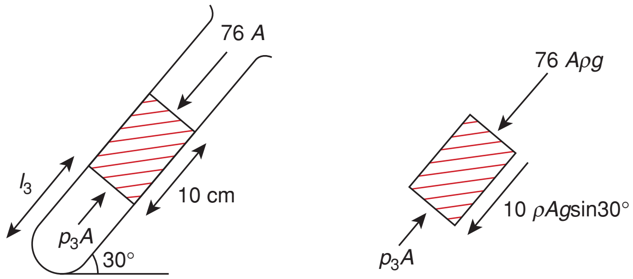
Here,

$$p_2 A = (76-10)\,A\rho g$$
$$p_2 = 66\rho g \text{ or } 66 \text{ cm of Hg}$$

Again applying Boyle’s law, we get

$$76\times 7\times A = 66\times l_2\times A$$
$$l_2 = 8.06 \text{ cm}$$

(c) When the test tube is held vertically at an angle of 30° with the horizontal as shown in Fig. 3.13(a). Then the forces acting on Hg column are depicted as shown in Fig. 3.13(b).



(a) (b)

Figure 3.13 (a) Test tube held vertically at an angle of 30° with the horizontal. (b) Forces acting on the Hg column.

Then

$$p_3 A = (76+10\sin 30°)\rho A g$$
$$p_3 = 81\rho g \text{ or } 81 \text{ cm of Hg}$$

From Boyle’s law

$$76\times 7A = 81\times l_3\times A$$
$$l_3 = 6.56 \text{ cm}$$

Solved Example 3-20

A 20L cylinder contains He at 20 atm and 300 K temperature. Helium in the container is used to fill balloons of 2 L at a pressure of 1 atm and $T = 300$ K. Find the number of balloons that can be filled.

Solution

Method 1:

Number of moles in the cylinder = n_{cylinder}

$$n_{\text{cylinder}} = \frac{pV}{RT} = \frac{20\times 20}{R\times 300} = \frac{400}{300R}$$

Number of moles in 1 balloon = n_{balloon}

Therefore, $$n_{\text{balloon}} = \frac{pV}{RT} = \frac{1\times 2}{R\times 300} = \frac{2}{300R}$$

Then, number of balloons $= \dfrac{400/300R}{2/300R} = 200$

This is a wrong answer!

Method 2: Gas flows only when there is pressure difference. Therefore, the moment the pressure in the cylinder is equal to pressure of gas, no moles will flow. Thus there will be moles in the gas cylinder that will not be used.

Let the moles left in the cylinder = n_{left}. Then

$$n_{\text{left}} = \frac{pV}{RT} = \frac{1\times 20}{R\times 300}$$

When $p = 1$ atm, no moles will flow. Therefore, number of balloons

$$= \frac{\dfrac{400}{300R} - \dfrac{20}{300R}}{\dfrac{2}{300R}} = \frac{280}{2} = 190$$

3.5 | PAYLOAD

Payload is defined as the maximum weight a balloon can lift. Consider the balloon and forces acting on it as shown in Fig. (3.14).

Let the volume of balloon = V
Pressure of gas inside balloon = p
Temperature of gas = T
Density of gas = ρ_{gas}
Then, mass of gas inside balloon = $(\rho_{\text{gas}})V$
For any object of volume V submerged in a fluid of density ρ_{fluid}, it will experience a buoyancy force upwards

$$\left|\vec{F}_{\text{buoyancy}}\right| = (\rho_{\text{fluid}})Vg$$

Therefore, in the given case

$$\left|\vec{F}_{\text{buoyancy}}\right| = (\rho_{\text{air}})Vg$$

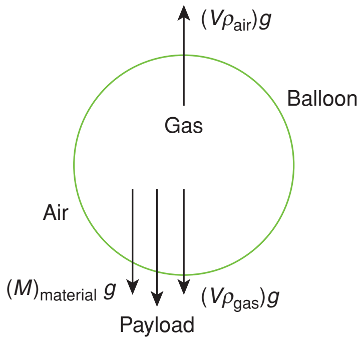


Figure 3.14 Payload.

Also balloon will be made of some material, so let us set the mass of material of balloon = M_{material}. Then because the balloon is rising up, the maximum weight this balloon can lift up = payload. Therefore, it acts downwards. Since we are calculating the maximum weight the balloon can carry, these forces should equal, that is

$$V\rho_{\text{air}}\, g = V\rho_{\text{gas}}\, g + M_{\text{material}} \times g + \text{Payload}$$

$$\text{Payload} = V(\rho_{\text{air}} - \rho_{\text{gas}})g - M_{\text{material}} \times g$$

$$\text{Payload} = V\left(\frac{p_{\text{air}} M_{\text{air}}}{RT_{\text{air}}} - \frac{p_{\text{gas}} M_{\text{gas}}}{R\,T_{\text{gas}}}\right)g - M_{\text{material}}\, g$$

Thus to increase the payload:

1. V should be the maximum.
2. Molecular weight of the gas should be least or lighter gas. So the best gas, theoretically, will be hydrogen with least molecular weight.
3. Temperature of gas should be high. Thus we heat the air and balloons are known as hot air balloons.

Note: In problems, when mass of material is not provided, neglect it.

3.6 | VARIATION OF PRESSURE WITH CHANGE IN DENSITY OF FLUID

To understand the variation of pressure with change in fluid, consider Fig. 3.15(a). To understand the variation of pressure with changing height of the column, we consider a small section of the column with height dh as shown in Fig. 3.15(b). Then the force diagram on the fluid column section is depicted in Fig. 3.15 (c).

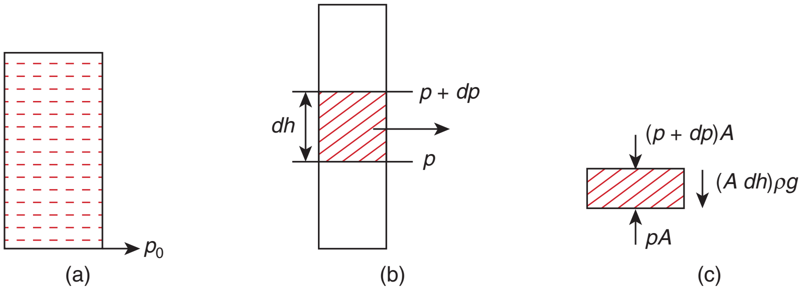


Figure 3.15 Variation of pressure with height in a fluid column.

Let the pressure at the bottom of the fluid column = p_0
At a height h, pressure = p
Area of cross-section = A

From the force diagram on the fluid column, we have

$$(p+dp)A + A\rho g dh = pA$$

$$dp = -\rho g dh$$

$$\frac{dp}{dh} = -\rho g$$

For liquid, density of liquid is constant. Therefore, $\int_{p_0}^{p} dp = -\int_{0}^{h} \rho g dh$

$$p - p_0 = -\rho g h$$

For gases, $\rho = \frac{pM}{RT}$, so

$$dp = -\frac{pMg}{RT}dh$$

$$\int_{p_0}^{p} \frac{dp}{p} = -\int_{h_0}^{h} \frac{Mg}{RT}dh$$

$$\ln\left(\frac{p}{p_0}\right) = \frac{-Mgh}{RT}$$

$$p = p_0 \rho^{-\frac{Mgh}{RT}}$$

Also,

$$\rho = \rho_0\, \rho^{-\frac{Mgh}{RT}}$$

where ρ = density at height $h = h$ and ρ_0 = density at height $h = 0$.

3.7 | FAULTY BAROMETER

In an ideal barometer (Fig. 3.16), pressure at point A should be equal to zero, but since perfect vacuum cannot be created, therefore, the pressure at A will not be zero. As a result, there will be an error in the measurement of pressure. For example consider a faulty barometer that reads 740 mm of Hg at an actual pressure of 750 mm of Hg. It reads 720 mm at the pressure of 728 mm of Hg. We need to determine the actual pressure when the barometer reads 750 m.

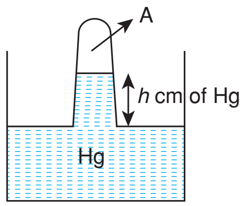
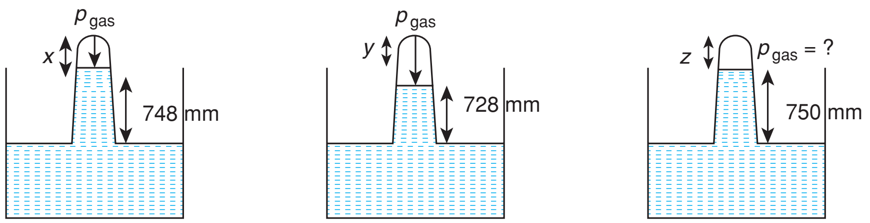


Figure 3.16 Barometer.

Consider the barometer in the first case, as shown in Fig. 3.17(a).



(a) (b) (c)

Figure 3.17 Faulty barometer.

Then the pressure of the gas is $p_{gas} = 750 - 740 = 10$ mm of Hg
Now in the second case [Fig. 3.17(b)], pressure of the gas is

$$p_{gas} = 728 - 720 = 8 \text{ mm of Hg}$$

To determine the actual pressure, when the barometer reads 750 mm of Hg, consider Fig. 3.17(c). The gas enclosed above Hg column is at constant T and has constant moles, therefore, we can apply Boyle's law.
The length of tube in the first case = $740 + x$
Therefore, the length of the tube in the second case will remain the same. So

$$y + 720 = 740 + x$$
$$y = 20 + x$$

Similarly length of tube in third case

$$z + 750 = 740 + x$$
$$z = x - 10$$

Applying Boyle's law in first and second case

$$10 \times x = 8(x + 20)$$
$$2x = 8 \times 20 \Rightarrow x = 80$$

Applying Boyle's law in second and third case

$$p_{\text{gas}} \times (x - 10) = 8(y)$$
$$p_{\text{gas}}\,(70) = 8(100)$$
$$p_{\text{gas}} = 11.42 \text{ mm of Hg}$$

Therefore, the actual pressure = 750 + 11.42 = 761.42 mm of Hg

---

3.8 | DALTON'S LAW OF PARTIAL PRESSURES

Gas mixtures obey the same laws as pure gases, so Boyle's law applies equally to both pure oxygen and to air. However, at times we need to consider the composition of a gas mixture, such as when we are concerned with a pollutant in the atmosphere. In a gas mixture, each of the components has the same volume and the same temperature.

In a mixture of non-reacting gases such as air, each gas contributes to the total pressure in proportion to the fraction (by moles) in which it is present. This contribution to the total pressure is called the **partial pressure** of the gas. It is the pressure the gas would exert if it were the only gas in a container of the same size at the same temperature.

The fact that pressure, like volume, does not depend on the identity of the gas was first suggested by John Dalton, author of modern atomic theory. Another gas law resulted. Dalton's law **states that the total pressure of a gas in a system is the sum of the partial pressures of each component gas**. The partial pressure of a specific gaseous element or compound is defined as the pressure due to that substance alone. Mathematically, this can be stated as

$$p_{\text{total}} = p_{\text{A}} + p_{\text{B}} + p_{\text{C}} + \ldots \qquad (3.21)$$

where p_{total} is the total pressure of the mixture, and $p_{\text{A}}, p_{\text{B}}, p_{\text{C}}$, etc. are the individual pressures of components A, B, C, etc.

When gases that do not react with water are prepared in the laboratory, they can be trapped over water by an apparatus like that shown in Fig. 3.18. Because of the way the gas is collected, it is saturated with water vapor and we say the gas is "wet". Water vapor in a mixture of gases has a partial pressure like that of any other gas.

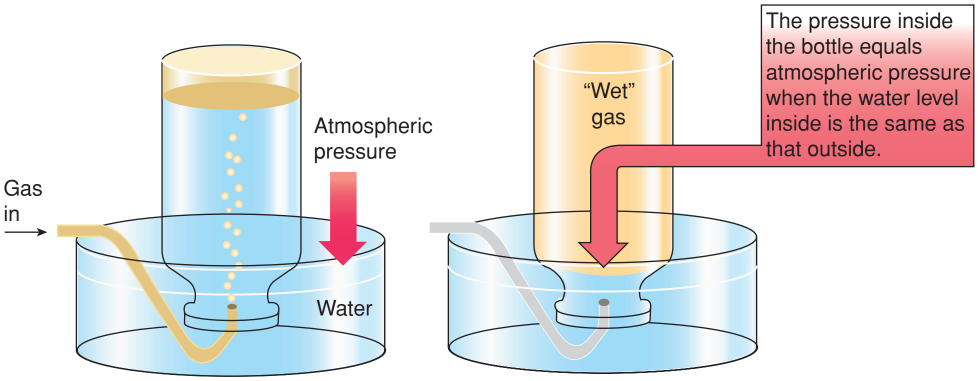

Gas in
Atmospheric pressure
Water
"Wet" gas
The pressure inside the bottle equals atmospheric pressure when the water level inside is the same as that outside.

Figure 3.18 Collecting a gas over water.

The vapor present in the space above *any* liquid always contains some of the liquid's vapor, which exerts its own pressure called the liquid's **vapor pressure** (**aqueous tension**). Its value for any given substance depends only on the temperature.

If we have adjusted the height of the collecting jar so that the water level inside matches that outside, the total pressure of the trapped gas equals the atmospheric pressure, so the value for p_{total} is obtained from the laboratory barometer. We, thus, calculate $p_{\text{dry gas}}$, which is the pressure that the gas would exert if it were dry (i.e., without water vapor in it) and inside the same volume that was used to collect it. Pressure exerted by saturated water vapor is called **aqueous tension**.The correction term is applied to the total pressure to obtain pressure of dry gas is

$$p_{\text{dry gas}} = p_{\text{total}} - \text{Aqueous tension} \tag{3.22}$$

where p_{total} is the sum of the partial pressure of non-reacting gases that are present together.

Relative Humidity

Humidity is the moisture content in the air. Relative humidity is defined as the ratio of the partial pressure of moisture in air to its vapor pressure. It is mathematically expressed as

$$\%\,\text{Relative humidity} = \frac{p_{H_2O}\ \text{in air}}{\text{Vapor pressure of } H_2O} \times 100 \tag{3.23}$$

The pressure of saturated vapors is independent of volume, so out of all the gas laws they obey only Dalton's law of partial pressure. If the %humidity in the air is higher, then the molecular weight of the mixture is lower. Also, humid air is lighter than dry air.

Solved Example 3-21

On a certain humid day, the mole fraction of water vapor in air at 25°C is 0.0287. If total pressure of air is 0.977 bar, calculate the partial pressure of water vapor in air and relative humidity if vapor pressure of water at 25°C is 0.0313 bar.

Solution

Here, mole fraction of H_2O $(x_{H_2O}) = 0.0287$, $p_{\text{total}} = 0.977$ bar. Therefore,

$$p_{H_2O} = x_{H_2O} \times p_{\text{total}} = 0.0287 \times 0.977 \text{ bar} = 0.028 \text{ bar}$$

and $$\%\,\text{Relative humidity} = \frac{p_{H_2O}\ \text{in air}}{\text{Vapor pressure of } H_2O} \times 100 = \frac{0.028}{0.313} \times 100 = 8.94\,\%$$

Solved Example 3-22

Assuming that dry air contains 79% N_2 and 21% O_2 by volume, what is the density of moist air at 25°C and 1.0 atm when the relative humidity is 60%? The vapor pressure of water at 25°C is 23.76 mm Hg.

Solution

From the given data we have, vapor pressure of H_2O = 0.6×23.76 mm Hg = 14.256 mm Hg
The number of moles of gas in 1 L dry air is

$$n_{\text{gas}} = \frac{pV}{RT} = \frac{1 \times 1}{0.0821 \times 298} = 0.0409\,\text{mol}$$

The number of moles of N_2 = 0.0409 × 0.79 = 0.0323 mol and mass of N_2 = 0.0323 × 28 = 0.9044 g
The number of moles of O_2 = 0.0409 × 0.21 = 0.0086 mol and mass of O_2 = 0.0086 × 32 = 0.2752 g
The number of moles of H_2O in 1 L of moist air is

$$n = \frac{pV}{RT} = \frac{0.0178 \times 1}{0.082 \times 298} = 7.28 \times 10^{-4}\ \text{mol}$$

Therefore, and mass of $H_2O = 7.6 \times 10^{-4} \times 18 = 0.01368$ g

Now, the density of moist air is

$$\rho = \frac{m_{N_2} + m_{O_2} + m_{H_2O}}{V} = \frac{0.9044 + 0.2752 + 0.01368}{1}$$

$$= 1.19 \text{ g L}^{-1}$$

Solved Example 3-23

What is the density of moist air with 90% relative humidity under the condition of 1 atm pressure and 25°C. The vapor pressure of water at 25°C is 23.7 torr and dry air has 76% N_2 and 24% O_2. Find the difference in the density of dry air and moist air at the given condition.

Solution

The vapor pressure of H_2O at 25°C is 23.7 mm of Hg. The average molecular weight is

$$M_{avg} = 0.76 \times 28 + 0.24 \times 32 = 21.28 + 7.68 = 28.96 \text{ g mol}^{-1}$$

The relative humidity is

$$\text{Relative humidity} = \frac{\text{Partial pressure of } H_2O}{\text{Vapor pressure of } H_2O} \times 100$$

where density is $\rho = \dfrac{pM_{air}}{RT}$

and $p_{H_2O} = 23.7 \times 0.9 = 21.33 \text{ torr} \approx 0.028 \text{ atm}$

Now, $M_{\text{moist air}} = (28.96 \times 0.972) + (18 \times 0.028) = 28.147 + 0.504 = 28.65 \text{ g mol}^{-1}$.

Substituting these values, we get the density as

$$\rho_{\text{moist air}} = \frac{pM_{\text{moist air}}}{RT} = \frac{1 \times 28.65}{0.0821 \times 298} = 1.171 \text{ g L}^{-1}$$

$$\rho_{\text{dry air}} = \frac{p_1 \times M_{\text{dry air}}}{RT} = \frac{1 \times 28.96}{0.0821 \times 298} = 1.1836 \text{ g L}^{-1}$$

The difference in density is

$$\Delta\rho = \rho_{\text{dry air}} - \rho_{\text{moist air}} = 1.1836 - 1.1710$$

$$= 0.0127 \text{ g L}^{-1}$$

Solved Example 3-24

On a humid summer day, the partial pressure of water in the atmosphere is 18 mm Hg. If the barometric pressure on this day is a high 766 mm Hg, what are the partial pressures of nitrogen and of oxygen if 78.0% of the dry atmosphere is composed of nitrogen molecules and 21.0% is oxygen? (1% of the dry atmosphere is composed of all other gases.)

Solution

The pressure of dry atmosphere is given as

$$p_{\text{(dry atmosphere)}} = p_{\text{tot}} - p_{H_2O} = 766 - 18 = 748 \text{ mm Hg}$$

The pressure of nitrogen and oxygen gases are calculated as follows:

$$p_{N_2} = \frac{78}{100} \times 748 = 583 \text{ mm Hg}$$

$$p_{O_2} = \frac{21}{100} \times 748 = 157 \text{ mm Hg}$$

Partial Pressure in Terms of Mole Fraction

The **mole fraction** is the ratio of the number of moles of a given component to the total number of moles of all components. Expressed mathematically, the mole fraction of substance A in a mixture of A, B, C, … , Z substances is

$$x_A = \frac{n_A}{n_A + n_B + n_C + \ldots + n_Z}$$

where x_A is the mole fraction of component A, and $n_A, n_B, n_C, \ldots, n_Z$ are the numbers of moles of each component, A, B, C, … , Z, respectively. The sum of all mole fractions for a mixture must always equal 1.

Note: Sometimes the mole fraction composition of a mixture is expressed on a percentage basis; we call it mole percent (mol%). The mole percent is obtained by multiplying the mole fraction by 100 mol%.

The total pressure of a mixture of gases can be extended to the ideal gas law. For example, consider a container with three constituent gases A, B and C with total pressure = p_{total}, volume = V and containing n_{A}, n_{B} and n_{C} moles of constituents A, B and C, respectively, at a temperature = T.

Let the pressure due to constituent A = p_{A} = partial pressure of A. For each of the constituent, total volume = V. Applying ideal gas equation on A, we have

$$p_{\text{A}}V = n_{\text{A}}\,RT$$

Similarly for B, $$p_{\text{B}}V = n_{\text{B}}RT$$

Similarly for C, $$p_{\text{C}}V = n_{\text{C}}RT$$

Applying ideal gas equation for the total mixture, we get

$$p_{\text{total}}V = (n_{\text{A}} + n_{\text{B}} + n_{\text{C}})RT$$

Dividing gas equation for A with gas equation for mixture, we get,

$$\frac{p_{\text{A}}}{p_{\text{total}}} = \frac{n_{\text{A}}}{n_{\text{A}} + n_{\text{B}} + n_{\text{C}}} = \frac{n_{\text{A}}}{n_{\text{total}}} = x_{\text{A}}$$

Therefore,

$$p_{\text{A}} = x_{\text{A}} \times p_{\text{total}}$$

$$p_{\text{B}} = x_{\text{B}} \times p_{\text{total}}$$

$$p_{\text{C}} = x_{\text{C}} \times p_{\text{total}}$$

Adding, we get

$$p_{\text{A}} + p_{\text{B}} + p_{\text{C}} = (x_{\text{A}} + x_{\text{B}} + x_{\text{C}})\,p_{\text{total}}$$

So, partial pressure of any component in a mixture = (mole fraction of component) × (total pressure).
As the sum of mole fractions is 1, we get

$$p_{\text{A}} + p_{\text{B}} + p_{\text{C}} = p_{\text{total}}$$

$$p_{\text{total}} = p_{\text{A}} + p_{\text{B}} + p_{\text{C}} = \frac{n_{\text{A}}RT}{V} + \frac{n_{\text{B}}RT}{V} + \frac{n_{\text{C}}RT}{V} \tag{3.24}$$

We see that, at a given temperature, the pressures of gases depend only on the total number of moles present. Therefore, partial pressure data can be used to calculate the mole fractions of individual gases in a gas mixture. Now, Eq. (3.26) can be rearranged as

$$p_{\text{total}} = (n_{\text{A}} + n_{\text{B}} + n_{\text{C}})\frac{RT}{V} \tag{3.25}$$

Dividing $p_{\text{A}} = n_{\text{A}}RT/V$ by Eq. (3.25) we get

$$\frac{p_{\text{A}}}{p_{\text{total}}} = \frac{n_{\text{A}}}{n_{\text{A}} + n_{\text{B}} + n_{\text{C}}}\,\frac{RTV}{RTV} = x_{\text{A}} \tag{3.26}$$

Thus, the mole fraction of a gas in a gas mixture is simply the ratio of its partial pressure to the total pressure. Equation (3.26) also gives us a simple way to calculate the partial pressure of a gas in a gas mixture when we know its mole fraction:

$$p_{\text{A}} = x_{\text{A}}\,p_{\text{total}}$$

The general equation for the *i*th fraction can be written as

$$p_i = x_i\,p_{\text{total}} \tag{3.27}$$

Solved Example 3-25

A sample of oxygen is collected over water at 20°C and a pressure of 738 mm Hg. Its volume is 310 mL. **(a)** What is the partial pressure of oxygen? **(b)** What would be its volume when dry at STP?

Solution

To calculate the partial pressure of the oxygen, we use Dalton's law. We will need the vapor pressure of water at 20°C, which is 17.5 mm Hg.

$$p_{O_2} = p_{\text{total}} - p_{\text{water vapor}} = (738 - 17.5)\text{ mm Hg} = 720\text{ mm Hg}$$

The answer to part **(a)** is that the partial pressure of O_2 is 720 mm Hg. For part **(b)**, we will begin by assembling the data.

Initial (1)		Final (2)
p	720 mm Hg (which is p_{O_2})	760 mm Hg (standard pressure)
V	310 mL	?
T	293 K (20.0°C + 273)	273 K (standard temperature)

We use these in the combined gas law equation:

$$\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$$

Solving for V_2 and rearranging the equation a bit we have

$$V_2 = V_1 \times \left(\frac{p_1}{p_2}\right) \times \left(\frac{T_2}{T_1}\right)$$

Now we can substitute values and calculate V_2.

$$V_2 = 310\text{ mL} \times \left(\frac{720\text{ mm Hg}}{760\text{ mm Hg}}\right) \times \left(\frac{273\text{ K}}{293\text{ K}}\right) = 274\text{ mL}$$

Thus, when the water vapor is removed from the gas sample, the dry oxygen will occupy a volume of 274 mL at STP.

Solved Example 3-26

Sulphur dioxide and oxygen react according to the equation $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$. If 50.0 g of $SO_2(g)$ is added to a flask resulting in a pressure of 0.750 atm, what will be the total pressure in the flask when a stoichiometric amount of oxygen is added? (Hint: This problem gives you more information than is needed.)

Solution

Since the stoichiometric ratio of the SO_2 and SO_3 are the same, the pressure in the flask after the reaction when the only substance in the flask is SO_3 will be the same as the pressure in flask when there is just SO_2, 0.750 atm. The pressure will be 1.125 atm when the O_2 is just added.

Solved Example 3-27

What is the mole fraction and the mole percent of oxygen in exhaled air if p_{O_2} is 116 mm Hg and p_{total} is 760 mm Hg?

Solution

$$x_{O_2} = \frac{p_{O_2}}{p_{\text{total}}} = \frac{116}{760} = 0.153 \text{ or } 15.3\%$$

Solved Example 3-28

A mixture containing 1.6 g of 0_2, 1.4g of N_2 and 0.4 g of He occupies a volume of 10 L at 27°C. Calculate the total pressure of the mixture and partial pressure of each compound.

Solution

Given that V = 10 L, T = 27°C = 300 K. The number of moles is

$$n_{\text{He}} = \frac{0.4}{4} = 0.1 \quad n_{\text{N}_2} = \frac{1.4}{28} = 0.05 \quad n_{\text{D}_2} = \frac{1.6}{32} = 0.05$$

Therefore, the total number of moles = 0.1 + 0.05 + 0.05 = 0.2

Using the ideal gas equation $pV = nRT$ and substituting the values, we get

$$pV = nRT \Rightarrow p \times 10 = 0.2 \times 0.082 \times 300 \Rightarrow p = 0.492 \text{ atm}$$

As partial pressure = total pressure × mole fraction, we have

$$p_{\text{He}} = 0.492 \times \frac{0.1}{0.2} = 0.246 \text{ atm}$$

$$p_{\text{N}_2} = 0.492 \times \frac{0.05}{0.2} = 0.123 \text{ atm}$$

$$p_{\text{O}_2} = 0.492 \times \frac{0.05}{0.2} = 0.123 \text{ atm}$$

Solved Example 3-29

Pressure of 1 g of an ideal gas A at 27°C is found to be 2 bar. When 2 g of another ideal gas B is introduced in the same flask, at same temperature the pressure becomes 3 bar. Find a relationship between their molecular masses.

Solution

Mass of gas A, w_{A} = 1 g and mass of gas B, w_{B} = 2 g. The pressure exerted by gas A = 2 bar and the total pressure due to both the gases = 3 bar. Here the temperature and volume remain constant. If M_{A} and M_{B} are the molar masses of the gases A and B, respectively, one can write,

$$p_{\text{A}}V = \frac{w_{\text{A}}}{M_{\text{A}}}RT \quad \text{and} \quad p_{\text{total}}V = \left(\frac{w_{\text{A}}}{M_{\text{A}}} + \frac{w_{\text{B}}}{M_{\text{B}}}\right)RT$$

Substituting the given values, we get

$$2 \text{ bar} \times V = \frac{1 \text{ g}}{M_{\text{A}}}RT \quad \text{and} \quad 3 \text{ bar} \times V = \left(\frac{1 \text{ g}}{M_{\text{A}}} + \frac{2 \text{ g}}{M_{\text{B}}}\right)RT$$

From the two equations, we get

$$\frac{3}{2} = \frac{\left(\dfrac{1 \text{ g}}{M_{\text{A}}} + \dfrac{2 \text{ g}}{M_{\text{B}}}\right)}{\left(\dfrac{1 \text{ g}}{M_{\text{A}}}\right)} = \frac{(M_{\text{B}} + 2M_{\text{A}})/(M_{\text{A}} \cdot M_{\text{B}})}{1/M_{\text{A}}}$$

$$= \frac{M_{\text{B}} + 2M_{\text{A}}}{M_{\text{B}}} = 1 + \frac{2M_{\text{A}}}{M_{\text{B}}}$$

This gives, $\dfrac{2M_{\text{A}}}{M_{\text{B}}} = \dfrac{3}{2} - 1 = \dfrac{1}{2} \Rightarrow \dfrac{M_{\text{A}}}{M_{\text{B}}} = \dfrac{1}{4} \Rightarrow M_{\text{B}} = 4M_{\text{A}}$

Thus, the molar mass of gas B is four times the molar mass of gas A.

3.9 | GRAHAM'S LAW OF EFFUSION AND DIFFUSION

Diffusion is the spontaneous mixing of the molecules of one gas, with molecules of another gas. For example, the aroma of the food, the fragrance of a perfume, etc. **Effusion**, on the other hand, is the gradual movement of gas molecules through a very tiny hole into a vacuum. The rates at which both of these processes occur depend on the speeds of gas molecules; the faster the molecules move, the more rapidly diffusion and effusion occur.

The Scottish chemist Thomas Graham (1805–1869) studied the rates of diffusion and effusion of a variety of gases through porous clay pots and through small apertures. Comparing different gases at the same temperature and pressure, Graham found that their rates of effusion were inversely proportional to the square roots of their densities. This relationship is now called **Graham's law**.

$$\text{Effusion rate}(r) = \frac{k}{\sqrt{\rho}} \quad \text{(when compared at the same } T \text{ and } p\text{)} \tag{3.28}$$

Graham's law is usually used in comparing the rates of effusion of different gases, so the proportionality constant can be eliminated and an equation can be formed by writing the ratio of effusion rates.

$$\frac{r_{\text{A}}}{r_{\text{B}}} = \frac{\sqrt{\rho_{\text{B}}}}{\sqrt{\rho_{\text{A}}}}$$

We know that the density of a gas is directly proportional to its molar mass. Therefore, we can re-express the equation as follows.

$$\frac{r_A}{r_B} = \frac{\sqrt{\rho_B}}{\sqrt{\rho_A}} = \sqrt{\frac{M_B}{M_A}}$$

where M_A and M_B are the molar masses of gases A and B. Molar masses also affect the rates at which gases undergo diffusion. Gases with low molar masses diffuse (and effuse) more rapidly than gases with high molar masses. Thus, hydrogen with a molar mass of 2 will diffuse more rapidly than methane, CH_4, with a molar mass of 16 g mol^{-1}.

If diffusion occurs at different pressures, p_A and p_B, then

$$\frac{r_A}{r_B} = \left(\frac{M_B}{M_A}\right)^{1/2} \times \frac{p_B}{p_A} \tag{3.29}$$

where $$r = \frac{\text{Volume diffused}\,(V)}{\text{Time interval}\,(t)} = \frac{\text{Moles diffused}\,(n)}{\text{Time interval}\,(t)} = \frac{\text{Distance travelled}\,(l)}{\text{Time interval}\,(t)}$$

Also, $r \propto (T)^{1/2}$, where T is temperature and $r \propto$ area of orifice (in case of effusion).

$$\text{Rate of effusion/diffusion} = \frac{\text{Moles diffused}}{\text{time}} = \frac{\text{Pressure drop}}{\text{time}} = \frac{\text{Volume diffused}}{\text{time}}$$

Consider the example of nitrogen gas (N_2) in a porous container (Fig. 3.19). Let us determine if oxygen (from the air) and nitrogen will diffuse. Here N_2 is at 1 atm and the air outside at one atmospheric pressure contains oxygen at 0.21 atm and nitrogen at 0.79 atm. So in this case N_2 will diffuse outside the container O_2 will go inside the container.

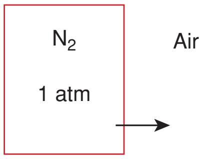


Figure 3.19 Diffusion of oxygen and nitrogen.

The rate of effusion can also be used for separation of isotopes with different molecular weights. For this purpose, a series of effusion steps in different containers are used.

Given that mass of isotope A, $M_A = 10$ and mass of isotope B, $M_B = 12$.

Let the initial mole ratio of A:B be $\frac{n_A}{n_B} = \frac{1}{2}$ and the required mole ratio $\frac{n_A}{n_B} = \frac{3}{4}$

In other words we want to enrich the lighter isotope A through multiple diffusions. The experimental set-up for this is depicted in Fig. 3.20.

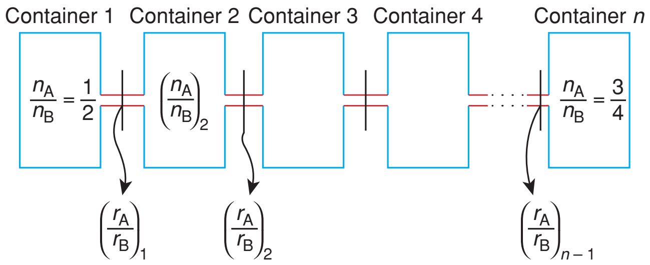

Container 1
Container 2
Container 3
Container 4
Container n
$\frac{n_A}{n_B} = \frac{1}{2}$
$\left(\frac{n_A}{n_B}\right)_2$
$\frac{n_A}{n_B} = \frac{3}{4}$
$\left(\frac{r_A}{r_B}\right)_1$
$\left(\frac{r_A}{r_B}\right)_2$
$\left(\frac{r_A}{r_B}\right)_{n-1}$

Figure 3.20 Experimental set-up for separation of isotopes through effusion.

Let the rate of effusion from first container to second be $\left(\frac{r_A}{r_B}\right)_1$, therefore,

$$\left(\frac{r_A}{r_B}\right)_1 = \left(\frac{p_A}{p_B}\right)_1 \left(\frac{M_B}{M_A}\right)^{\frac{1}{2}}$$

$$\left(\frac{r_A}{r_B}\right)_1 = \left(\frac{n_A}{n_B}\right)_1 \left(\frac{M_B}{M_A}\right)^{\frac{1}{2}} \tag{3.30}$$

Let the rate of effusion from second container to third container be $\left(\frac{r_A}{r_B}\right)_2$, therefore,

$$\left(\frac{r_A}{r_B}\right)_2 = \left(\frac{p_A}{p_B}\right)_2 \left(\frac{M_B}{M_A}\right)^{\frac{1}{2}}$$

$$\left(\frac{r_A}{r_B}\right)_2 = \left(\frac{n_A}{n_B}\right)_2 \left(\frac{M_B}{M_A}\right)^{\frac{1}{2}} \tag{3.31}$$

Also as container 2 is evacuated, in the beginning.

$$\left(\frac{n_A}{n_B}\right)_2 = \left(\frac{r_A}{r_B}\right)_1 \tag{3.32}$$

Therefore, from above Eqs. 3.30 to 3.32, we have

$$\left(\frac{r_A}{r_B}\right)_2 = \left(\frac{n_A}{n_B}\right)_1 \left(\frac{M_B}{M_A}\right)^{\frac{2}{2}}$$

Similarly for the n^{th} container

$$\left(\frac{r_A}{r_B}\right)_{n-1} = \left(\frac{n_A}{n_B}\right)_1 \left(\frac{M_B}{M_A}\right)^{\frac{(n-1)}{2}}$$

Also $$\left(\frac{r_A}{r_B}\right)_{n-1} = \left(\frac{n_A}{n_B}\right)_n$$

Therefore,

$$\left(\frac{n_A}{n_B}\right)_1 \left(\frac{M_B}{M_A}\right)^{\left(\frac{n-1}{2}\right)} = \left(\frac{n_A}{n_B}\right)_n$$

$$\log\left(\frac{n_A}{n_B}\right)_1 + \frac{(n-1)}{2}\log\left(\frac{M_B}{M_A}\right) = \log\left(\frac{n_A}{n_B}\right)_n$$

The given and required molar ratio is

$$\left(\frac{n_A}{n_B}\right)_1 = \frac{1}{2}$$

$$\left(\frac{n_A}{n_B}\right)_n = \frac{3}{4}$$

and $M_A = 10$, $M_B = 12$. Substituting values, we get

$$\log\left(\frac{1}{2}\right) + \frac{(n-1)}{2}\log\left(\frac{12}{10}\right) = \log\left(\frac{3}{4}\right)$$

Thus we can find "n" or the number of steps $(n-1)$ to get the required mole ratio.

Variation of Pressure inside a Container during Effusion of a Gas

If the given pressure inside a container is p_0, we can determine the pressure inside the container at a time $t = t_0$ as follows.

Let the molecular weight of gas be M. Let the pressure at any time $t = t_1$ be p_1. Then

$$(\text{rate})_t = k\frac{p_1}{\sqrt{M}}$$

where k is a constant.

The drop in pressure with time is $\frac{dp}{dt}$.

Therefore, total pressure drop with time is

$$-\int_{p_0}^{p_0}\frac{dp_1}{p_1} = \int_0^t k\frac{dt}{\sqrt{M}} = \ln\left(\frac{p}{p_0}\right) = \frac{kt}{\sqrt{M}}$$

Therefore,
$$p = p_0 e^{-\frac{k}{\sqrt{M}}t}$$

Thus during effusion/diffusion, pressure inside the container falls exponentially as shown in Fig. 3.21.

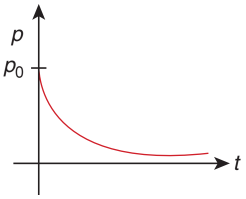


Figure 3.21 Variation in pressure of gas inside a container due to effusion.

Solved Example 3-30

When you look directly up at the sky, you are actually looking through a very tall, transparent column of air that extends from the surface of the earth thousands of kilometers into space. If the air in this column were liquefied, how tall would it be? The density of liquid air is 0.89 g mL^{-1}.

Solution

1 atm = 1033.228 g cm^{-2}

Column height = $(1033.228\,\text{g cm}^{-2})\left(\frac{1\,\text{cm}^3}{0.89\,\text{g}}\right)$ = 1,200 cm = 12 m

---

Solved Example 3-31

A small quantity of gaseous NH_3 and HBr are introduced simultaneously into the opposite ends of an open tube that is 1 m long. Calculate the distance of the while solid NH_4Br formed from the end that was used to introduce NH_3.

Solution

By Graham's law of diffusion

$$\frac{r_{NH_3}}{r_{HBr}} = \sqrt{\frac{M_{HBr}}{M_{NH_3}}} = \sqrt{\frac{81}{17}} = 2.18$$

Thus, NH_3 travels 2.18 times faster than HBr. In other words, NH_3 will travel 2.18 cm in the same time in which HBr travels 1 cm. Given that the length of the tube = 100 cm.

Therefore, distance travelled in the tube by

$$NH_3 = \frac{2.18}{2.18+1}\times 100 = 68.55\,\text{cm}$$

Thus, NH_4Br will first appear at a distance of 68.55 cm from NH_3 end.

Solved Example 3-32

Pure O_2 diffuses through an aperture in 224 s, whereas mixture of O_2 and another gas containing 80% O_2 diffuses from the same in 234 s under similar condition of pressure and temperature. What is molecular weight of gas?

Solution

The gaseous mixture contains 80% O_2 and 20% gas. The average molecular weight of mixture is

$$M_{\text{mix}} = \frac{32 \times 80 + 20 \times m}{100} \qquad (1)$$

as $M_{\text{mix}} = \sum M_i x_i$ where x_i = mole fraction. Now for diffusion of gaseous mixture and pure O_2

$$\begin{aligned} \frac{r_{O_2}}{r_{\text{mix}}} &= \sqrt{\frac{M_{\text{mix}}}{M_{O_2}}} \Rightarrow \frac{V_{O_2}}{V_{\text{mix}}} \times \frac{t_{\text{mix}}}{t_{O_2}} \\ &= \sqrt{\frac{M_{\text{mix}}}{32}} \Rightarrow \frac{1}{224} \times \frac{234}{1} = \sqrt{\frac{M_{\text{mix}}}{32}} \qquad (2) \end{aligned}$$

On solving, we get $M_{\text{mix}} = 34.92$ g mol^{-1}. Thus, substituting in Eq. (1), we get molecular weight of gas (m) as

$$m = \frac{34.92 \times 100 - 32 \times 80}{20} = 46.6 \text{ g mol}^{-1}$$

Solved Example 3-33

Equal volumes of two gases A and B diffuse through a porous pot in 20 s and 10 s, respectively. If the molar mass of A be 80 g mol^{-1}, find the molar mass of B.

Solution

Let V be the volume of the two gases diffused out. Then according to Graham's law

$$\frac{r_A}{r_B} = \frac{V/20\,\text{s}}{V/10\,\text{s}} = \sqrt{\frac{M_B}{M_A}}$$

where rate (r) = volume diffused/time interval. Simplifying, we get

$$\frac{10}{20} = \sqrt{\frac{M_B}{80}} \Rightarrow M_B = \frac{100}{400} \times 80 = 20 \text{ g mol}^{-1}$$

3.10 | KINETIC THEORY OF GASES

The **kinetic molecular theory of gases** was proposed to understand at molecular level in gases for their conformity to gas laws. The theory consisted of a set of postulates that describe the makeup of an ideal gas.

Postulates

1. A gas consists of large number of particles, identical in shape and size, which are all spherical in shape.
2. The gas particles themselves occupy a net volume so small with respect to the volume of their container that their contribution to the total volume can be ignored. Hence, they are considered as point masses. This is the reason why they are highly compressible.
3. All molecules are in a state of constant random motion and during their motion they collide with each other and with the walls of the container. The particles often collide in perfectly elastic collisions with themselves and with the walls of the container, thereby exerting pressure. During collisions, there is exchange of energy leading to change in individual energies but the total energy remains constant. They move in straight lines between collisions neither attracting nor repelling each other.
4. The temperature of a gas is related to the average kinetic energy of the gas molecules. The average kinetic energy is directly proportional to the absolute temperature. When the volume is kept constant, an increase in temperature leads to an increase in pressure. The increase in temperature in turn increases the kinetic energy of the particles which then hit the walls of the container exerting pressure. Also, at the same temperature, different gases have the same average kinetic energy.
5. At a given time, different particles in a gas have different kinetic energies as their energies change when they collide.

6. **Absolute zero:** The kinetic theory found that the temperature is proportional to the average kinetic energy of the molecules.

$$T \propto \text{Average molecular knietic energy} \propto \frac{1}{2}mu^2 \tag{3.33}$$

If the average molecular kinetic energy becomes zero, the temperature must also become zero. But mass (m) cannot become zero, so the only way that the average molecular kinetic energy can be zero is if v goes to zero. A particle cannot move any slower than it does at a dead standstill, so if the particles stop moving entirely, the substance is as cold as anything can get. It is at absolute zero.

The force of interaction between any two gas particles is zero.

Prediction of Gas Laws

The kinetic theory explains the properties of gases as well as the gas laws described earlier.

1. **Boyle's law:** If we compress a gas without changing its temperature, the average kinetic energy of the gas particles stays the same. There is no change in the speed with which the particles move, but the volume of the container is smaller. Thus the particles travel from one end of the container to the other in a shorter time and hit the walls more often. Any increase in the frequency of collisions with the walls must lead to an increase in the pressure of the gas. Thus the pressure of a gas increases as the volume of the gas decreases.
2. **Gay–Lussac's law:** The kinetic theory tells us that increasing the temperature increases the average velocity of gas particles. At higher velocities, the particles strike the container's walls more frequently and with greater force. If the volume remains the same, the *area* being struck remains the same, so the force per unit area (the pressure) must increase. Thus, the kinetic theory explains how the pressure of a fixed amount of gas is proportional to temperature (at constant volume).
3. **Charles' law:** The kinetic theory predicts that increasing the temperature of a gas should increase the pressure if the volume does not change. However, suppose we wished to keep the pressure constant when we raised the temperature, we could only do this if we allowed the gas to expand. Therefore, a gas expands with increasing T in order to keep p constant, which is another way of saying that V is proportional to T at constant p.
4. **Dalton's law of partial pressures:** The law of partial pressures is actually evidence for that part of the kinetic theory that states that particles of an ideal gas moving in straight lines between collisions, neither attracting nor repelling each other. Only if the molecules traveled in straight lines with no attractions or repulsions would their individual pressures not be influenced by near misses or by collisions between the molecules. By not interacting with each other, the molecules act *independently*, so each gas behaves as though it were alone in the container and the partial pressures of the gases add up in a simple way to give the total pressure.

Derivation of Kinetic Gas Equation

The kinetic gas equation gives the relationship between temperature ad average kinetic energy and is usually written in the form

$$pV = \frac{1}{3}mnu^2$$

where p is the pressure exerted by the gas, V is the volume of the gas, m is the mass of each molecule of the gas, n is total number of molecules present in volume V and u is the root mean square speed of the gas.

Now, $$pV = \frac{1}{3}mnu^2 = \frac{2}{3}\times\frac{1}{2}mnu^2 = \frac{2}{3}\times\frac{1}{2}Mu^2$$

where $m \times n = M$ is the total mass of the gas. But $(1/2)Mu^2$ = kinetic energy of the gas. Therefore,

$$pV = \frac{2}{3}\text{K.E.}$$

or $$\text{K.E.} = \frac{3}{2}pV \text{ for 1 mol of the gas}$$

But for 1 mol of the gas, the ideal gas equation is $pV = RT$. Thus,

$$\text{K.E.} = \frac{3}{2}RT \text{ for 1 mol of the gas} \tag{3.34}$$

To get average kinetic energy per molecule, divide both sides of Eq. (3.34) by the Avogadro's number, N_A, that is, the number of molecules present in 1 mol of the gas. Thus, we have

$$\text{Average K.E.} = \frac{3}{2}\frac{RT}{N_A}$$

or $$\text{K.E.} = \frac{3}{2}kT \tag{3.35}$$

where $k = R/N_A$ is called Boltzmann constant. From Eq. (3.35), we observe that

Average K.E. $\propto$ Absolute temperature of the gas irrespective of the nature of the gas

Kinetic Energy of Gas and Average, Most Probable and Root Mean Square Speeds

The molecules of gases are always in motion and collide with each other and with the walls of the container. These collisions cause the speed and kinetic energies of the individual molecules to change. At a given temperature, if n_1 molecules of a gas have speed u_1, n_2 molecules have speed u_2 and so on, then the total kinetic energy of gas molecules is given by

$$\text{K.E.} = \frac{1}{2}m(n_1u_1 + n_2u_2 + n_3u_3 + \ldots)^2$$

where m is the mass of gas molecule. Then the average kinetic energy $(\overline{\text{K.E.}})$ of the gas will be given by

$$\overline{\text{K.E.}} = \frac{1}{2}\frac{m(n_1u_1^2 + n_2u_2^2 + n_3u_3^2 + \ldots)}{(n_1 + n_2 + n_3 + \ldots)} \tag{3.36}$$

If the term $\dfrac{(n_1u_1^2 + n_2u_2^2 + n_3u_3^2 + \ldots)}{(n_1 + n_2 + n_3 + \ldots)} = u_{\text{rms}}^2$, then substituting in Eq. (3.36), we get

$$\overline{\text{K.E.}} = \frac{1}{2}mu_{\text{rms}}^2 \tag{3.37}$$

where u_{rms} is known as the root mean square (rms) velocity and is given by

$$u_{\text{rms}} = \sqrt{\frac{(n_1u_1^2 + n_2u_2^2 + n_3u_3^2 + \ldots)}{(n_1 + n_2 + n_3 + \ldots)}} = \left[\frac{\sum n_iu_i^2}{\sum n_i}\right]^{1/2} \tag{3.38}$$

It is calculated by first taking squares of individual velocities, taking their mean and then the square root of the mean. The root mean square velocity is related to the temperature by the relation

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}} \tag{3.39}$$

The average kinetic energy of gas molecules, however, is constant at a given temperature and is related to the absolute temperature by the relation

$$\overline{\text{K.E.}} = \frac{3RT}{2N_A} = \frac{3}{2}kT \tag{3.40}$$

where k is the Boltzmann constant = 1.38×10^{-23} J K^{-1}.

Note: The average kinetic energy per mole $(\text{K.E.})_{\text{avg}}$ is equal to kinetic energy per molecule $(\overline{\text{K.E.}})$ multiplied by the Avogadro's number (N_A).

$$(\text{K.E.})_{\text{avg}} = N_A \times \frac{3}{2}kT = \frac{3}{2}RT$$

In principle, we can find the **average speed** (u_{avg}) of the molecules in a gas by taking the arithmetic mean of the speeds of different molecules of the gas.

$$u_{\text{avg}} = \frac{(n_1u_1 + n_2u_2 + n_3u_3 + \ldots)}{(n_1 + n_2 + n_3 + \ldots)} = \frac{\sum n_iu_i}{\sum n_i}$$

The average speed is related to the temperature by the relation

$$u_{\text{avg}} = \sqrt{\frac{8RT}{\pi M}} \tag{3.41}$$

The **most probable speed** (u_{mp}) of the gas molecules is the speed possessed by maximum number of molecules at a given temperature. It cannot be expressed in terms of speed of individual molecules as in the case of average and root mean square speed. It is related to the absolute temperature by the expression:

$$u_{\text{mp}} = \sqrt{\frac{2RT}{M}} \tag{3.42}$$

A molecule is more likely to have speed u_{mp} than any other speed, but some molecules will have speeds that are many times the most probable speed.

Note: Total kinetic energy is the sum of translational, vibrational and rotational kinetic energies. The total kinetic energy is equal to the translational kinetic energy for monoatomic gases as they do not possess vibrational and rotational motion but only have translational motion.

Relation Between Different Types of Molecular Speeds

The three types of molecular speeds of gas molecules are related to each other as:

$$u_{\text{mp}} : u_{\text{avg}} : u_{\text{rms}} = \sqrt{\frac{2RT}{M}} : \sqrt{\frac{8RT}{\pi M}} : \sqrt{\frac{3RT}{M}} = \sqrt{2} : \sqrt{\frac{8}{\pi}} : \sqrt{3} = 1.414 : 1.596 : 1.732 = 1 : 1.128 : 1.224 \tag{3.43}$$

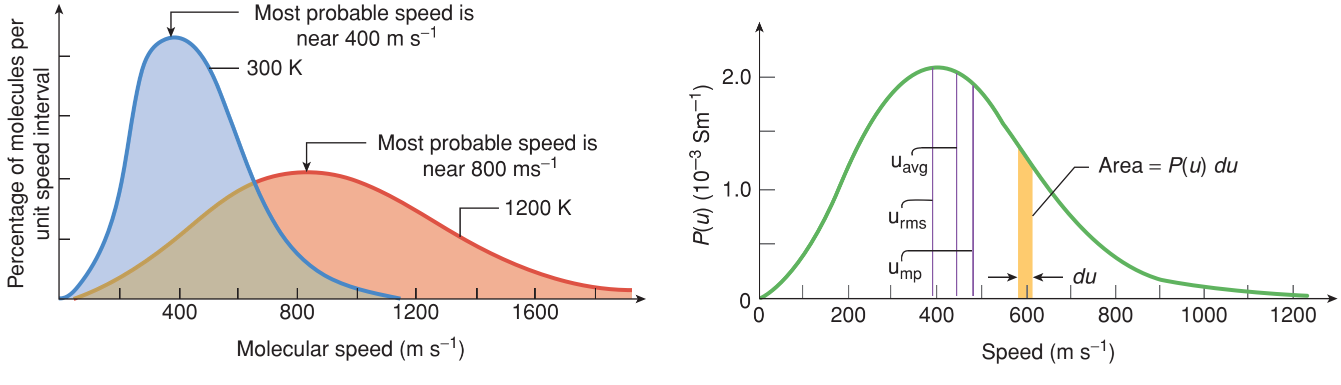
At a given temperature, the three molecular speeds can be arranged in the order: $u_{\text{mp}} > u_{\text{avg}} > u_{\text{rms}}$.

Note: Average speed = 0.921 × Root mean square speed
Most probable speed = 0.817 × Root mean square speed

Maxwell–Boltzmann Distribution of Molecular Speeds

Speed of gas particles keeps changing due to collision of gas particles with the walls of the container and with other molecules. Therefore, speed does not remain constant, but the distribution of speed, that is fraction of molecules having speed in a particular range remains constant for an isolated system. (An isolated system is one in which temperature, molar mass, pressure, volume and number of moles, etc. are constant.)

For conditions of low gas density, the distribution of speeds within a large collection of molecules at a constant temperature was calculated by the Scottish physicist James Clerk Maxwell (1831–1879). Figure 3.22(a) displays the Maxwell speed distribution curves for O_2 gas at two different temperatures. When the temperature is 300 K, the maximum in the curve indicates that the most probable speed is about 400 m s^{-1}. At a temperature of 1200 K, the distribution curve shifts to the right, and the most probable speed increases to about 800 m s^{-1}.



(a)

(b)

Figure 3.22 (a) Maxwell distribution curves for molecular speeds in oxygen gas at temperatures of 300 K and 1200 K. (b) Maxwell speed distribution for oxygen molecules at $T = 300$ K with three characteristic speeds marked.

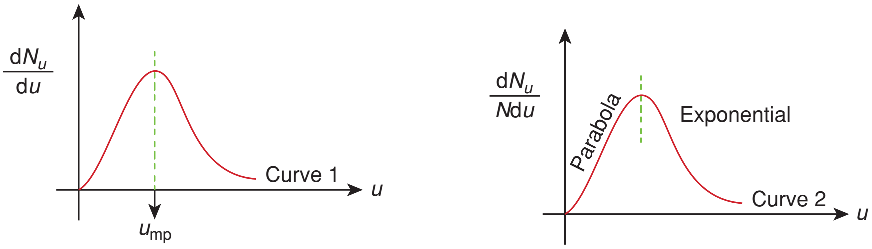
Important features of the distribution curve are as follows:

1. The fraction of molecules having too low or too high speed is very small.
2. At a certain speed, the fraction of molecules possessing it is the maximum. This is known as the **most probable speed**.
3. The most probable speed is the speed possessed by the maximum number of molecules of the gas at a given temperature and corresponds to the peak in the curve.

Maxwell derived an equation for distribution of speed using the concept of probability. Then the fraction of molecules having velocity between u and u + du is

$$\frac{dN_u}{N} = 4\pi\left(\frac{M}{2\pi RT}\right)u^2 e^{-\left(\frac{Mu^2}{2RT}\right)}du$$

Here N is the total number of molecules, N_u is the number of molecules having velocity between u and u + du, where du is small change in velocity. Then the Maxwell's distribution curves are plotted between number of molecules having velocity between u and u + du per unit change in velocity as shown in Figs. 3.23(a) and (b).



(a)

(b)

Figure 3.23 Maxwell's distribution curves. (a) Curve 1. (b) Curve 2.

Total area under small part of curve 1 represents number of molecules moving with velocity between u and u + du. Therefore

$$\text{Area} = \frac{dN_u}{du} \times du = dN_u$$

Total area under curve 1 represents total number of molecules

$$\text{Total area } = \int \frac{dN_u}{du} \times du = \int dN_u = N$$

Area under small part of curve 2 represents fraction of molecules having velocity between u and $u + du$

$$\text{Area} = \frac{dN_u}{N du} \times du = \frac{dN_u}{N}$$

$$\text{Total area} = \int \frac{dN_u}{N} = \int \frac{dN_u}{N} = \frac{N}{N} = 1$$

Thus, the total area under curve 2 = 1.
The graph curve 2 can be divided into two parts:

1. **Parabolic part:** Near the origin, that is, in the lower velocity range, parabolic term u^2 dominates. In this range, the exponential term $\left(e^{-\frac{Mu^2}{2RT}}\right)$ is almost equal to 1. As u increases, dN_u increases because $dN_u \propto u^2$.
2. **Exponential part:** In high velocity region, the exponential term dominates and the parabolic term (u^2) is almost constant. As u increases, dN_u decreases as $dN_u \propto e^{-u^2}$.

   Maxwell's speed distribution law can be stated as

$$P(u) = 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} u^2 e^{-Mu^2/2RT} \tag{3.44}$$

Here M is the **molar mass** of the gas, R is the gas constant, T is the gas temperature, and u is the molecular speed. It is this equation that is plotted in Fig. 3.23(b). The quantity $P(u)$ in Eq. (3.44) and Fig. 3.22(b) is a *probability distribution function:* For any speed u, the product $P(u)$ du (a dimensionless quantity) is the fraction of molecules with speeds in the interval du centered on speed u. This fraction is equal to the area of a strip with height $P(u)$ and width du. The total area under the distribution curve corresponds to the fraction of the molecules whose speeds lie between zero and infinity. All molecules fall into this category, so the value of this total area is unity; that is,

$$\int_0^\infty P(u)\, du = 1 \tag{3.45}$$

The fraction (f) of molecules with speeds in an interval of, say, u_1 to u_2 is then

$$f = \int_{u_1}^{u_2} P(u)\, du \tag{3.46}$$

We know that the **most probable speed** (u_{mp}) is related to the temperature by the expression

$$u_{\text{mp}} = \sqrt{\frac{2RT}{M}}$$

This relation is used to determine the effect of nature (molecular mass) of the gas and temperature on the molecular speeds:

1. Since most probable speed is inversely proportional to the molecular mass, the lighter gases will move faster than heavier ones at the same temperature.
2. The Maxwell distribution curve at two different temperatures [Fig 3.22(a)] shows that the curves undergo following changes with increase in temperature:
   - (a) The entire curve shifts to the right.
   - (b) The maximum shifts to higher speed values.
   - (c) The spread of molecular speed increases.
   - (d) The number of molecules having most probable speed decreases.
   - (e) The fraction of molecules having lower speed decreases.

Effect of Temperature

With increase in temperature, u_{mp} increases, that is, peak is shifted towards right hand side. Hence height of the peak decreases because area under the curve is constant. Therefore, of molecules having speed equal to u_{mp} decreases. In low velocity range:

$$dN_u \propto \frac{1}{T^{3/2}}$$

As temperature increases, the number of molecules having low velocity decreases.

In high velocity range:

$$dN_u \propto e^{\frac{-1}{T}}$$

As temperature increases, the number of molecules having high velocity increases (Fig. 3.24).

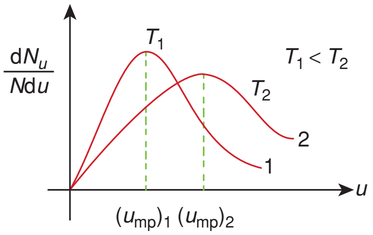


Figure 3.24 Effect of temperature in low and high velocity range.

Effect of Molar Mass

With increase in molar mass, u_{mp} decreases, that is, the peak is shifted towards left. Hence, the height of peak increases as the total area of the curve is constant. Therefore, total number of molecules having speed equal to u_{mp} increases.

In low velocity region:

$$dN_u \propto M^{\frac{3}{2}}$$

As M increases, the number of molecules having lower speed increases.

In high velocity region:

$$dN_u \propto e^{-M}$$

As M increases, the number of molecules having high velocity decreases (Fig. 3.25).

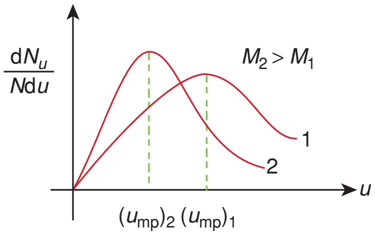


Figure 3.25 Effect of molar mass in low and high velocity range.

Note: Distribution of speed will be the same for two gases if their M/T ratio is the same.

Derivation of Different Types of Molecular Speeds

Most Probable Speed (u_{mp})

We know that

$$\frac{d}{du}\left(\frac{dN_u}{du}\right) = 0$$

$$\frac{d}{du}\left(4\pi N\left(\frac{M}{2\pi RT}\right)\right)^{\frac{3}{2}} u^2 e^{-\frac{Mu^2}{2RT}} = 0$$

$$4\pi N\left(\frac{M}{2\pi RT}\right)^{\frac{3}{2}}\left[2ue^{-\frac{Mu^2}{2RT}}-\frac{2Mu^3}{2RT}e^{-\frac{Mu^2}{2RT}}\right]=0$$

Solving, we get

$$u=\sqrt{\frac{2RT}{M}}\Rightarrow u_{\text{mp}}=\sqrt{\frac{2RT}{M}}$$

Average Speed (u_{avg})

$$\begin{aligned}u_{\text{avg}}&=\frac{u_1+u_2+\ldots u_N}{N}\\&=\frac{u_1(\mathrm{d}N_{u1})+u_2(\mathrm{d}N_{u2})+\ldots u_i(\mathrm{d}N_{ui})}{N}\\&=\sum\frac{u_i(\mathrm{d}N_{ui})}{N}\\&=\int_0^\infty\frac{u\mathrm{d}Nu}{N}=\int u^3\times4\pi\left(\frac{M}{2\pi RT}\right)^{\frac{3}{2}}e^{-\frac{Mu^2}{2RT}\mathrm{d}u}\end{aligned}$$

Solving, we get

$$u_{\text{avg}}=\sqrt{\frac{8RT}{\pi M}}$$

Root Mean Square Speed (u_{rms})

$$u_{\text{rms}}=\sum u_i^{\,2}\frac{\mathrm{d}N_{ui}}{N}$$

Solving, we get

$$u_{\text{rms}}=\sqrt{\frac{3RT}{M}}$$

Derivation of Kinetic Gas Equation

Let us consider a cubic container of length l with one particle of mass = m, travelling with speed u_x in x-direction (Fig. 3.26).

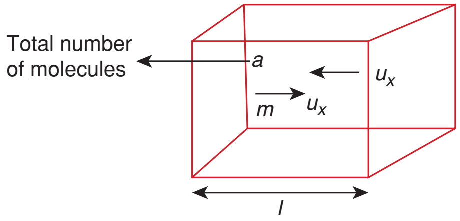


Figure 3.26 Cubic container with moving particle.

Now since all collisions are elastic, the speed of particle after collision with the wall of the container = u_x in the opposite direction. Therefore, change in momentum of the molecule

$$\Delta p_{\text{molecule}}=m(u_x)-m(+u_x)=2mu_x$$

Whenever a collision occurs, the total change of momentum of bodies involved in collision = 0, that is,

$$\begin{aligned}\Delta p_{\text{molecule}}+\Delta p_{\text{wall}}&=0\\\Delta p_{\text{wall}}&=2mu_x\end{aligned}$$

Total time taken by molecule to return = $2\left(\frac{l}{u_x}\right)$

Therefore, number of collisions made by the molecule in one second = $\left(\frac{u_x}{2l}\right)$

Then, total change in momentum of wall by one molecule per unit time $= 2mu_x \times \frac{u_x}{l} = \frac{mu_x{}^2}{l}$

Therefore, change in momentum of wall by all molecules per unit time $= \frac{m\sum u_x{}^2}{l}$

(Because all particles will have different u_x.)
The force applied on the wall is equal to rate of change of momentum $= \frac{m\sum u_x{}^2}{l}$
The pressure is given by

$$p = \frac{F}{A} = \frac{M\sum u_x^2}{l} \times \frac{1}{l^2} = \frac{M\sum u_x^2}{l^3} = \frac{M\sum u_x^2}{V}$$

where V is the volume of the container. Then

$$pV = M\sum u_i^2$$

$$\vec{u} = u_x\hat{i} + u_y\hat{j} + u_z\hat{j}$$

Thus velocity of any molecule is

$$u^2 = u_x^2 + u_y^2 + u_z^2$$

For all molecules

$$\sum u^2 = \sum u_x^2 + \sum u_y^2 + \sum u_z^2$$

Since the motion of molecules is completely random, we have

$$\sum u_x^2 = \sum u_y^2 = \sum u_z^2$$

Therefore,

$$\sum u_i^2 = \frac{\sum u^2}{3}$$

Thus,

$$pV = \frac{1}{3}M\sum u^2 \tag{3.47}$$

$$pV = \frac{1}{3}M\left(\frac{\sum u^2}{a}\right)$$

where a is the total number of molecules. Then

$$pV = \frac{1}{3}Ma\,u_{\text{rms}}^2$$

We can go a step further and derive the ideal gas equation for one molecule as

$$pV = \frac{1}{3}\left(\frac{M}{N_{\text{A}}}\right)a\left(\frac{3RT}{M}\right) = \left(\frac{a}{N_{\text{A}}}\right)RT$$

For n number of moles, we get the ideal gas equation as

$$pV = nRT$$

The expression for kinetic energy of gas molecules can be derived from Eq. (3.49).

$$pV = \frac{1}{3}M\sum u^2$$

$$M\sum u^2 = 3pV$$

$$\frac{1}{2}M\sum u^2 = \frac{3}{2}pV$$

So total kinetic energy

$$\text{K.E.} = \frac{3}{2}pV = \frac{3}{2}nRT$$

Note: K.E. of any gas can only be changed by change in temperature.

Average K.E. per mole $= \dfrac{\frac{3}{2}nRT}{n} = \dfrac{3}{2}RT$

Average K.E. per molecule $= \dfrac{3}{2}\dfrac{RT}{N_A} = \dfrac{3}{2}\left(\dfrac{R}{N_A}\right)T = \dfrac{3}{2}kT$

Here k is the Boltzmann constant = $1.38 \times 10^{-23}\ \text{JK}^{-1}$

Note: Potential energy of ideal gas is exactly 0. Therefore, K.E. = total energy for an ideal gas.

Maxwell distribution of kinetic energy can be obtained as follows. We know that total energy

$$E = \text{K.E.}$$

$$E = \frac{1}{2}Mu^2 \Rightarrow u^2 = \frac{2E}{M}$$

$$2u\,du = \frac{2}{M}dE \Rightarrow udu = \frac{dE}{M}$$

Then on substituting in the Maxwell's equation

$$\frac{dN_u}{N} = 4\pi\left(\frac{M}{2\pi RT}\right)^{\frac{3}{2}} e^{-\frac{Mu^2}{2RT}}u^2du$$

$$\frac{dN_E}{N} = 4\pi\left(\frac{M}{2\pi RT}\right)^{\frac{3}{2}} e^{-\frac{M}{2RT}\frac{2E}{M}}\sqrt{\frac{2E}{M}}.\frac{dE}{M}$$

$$= 2\pi\left(\frac{1}{\pi RT}\right)^{\frac{3}{2}} e^{-\frac{E}{RT}}\sqrt{E}dE$$

The fraction of molecules with molecular mass M at temperature T having speed from u_{mp} to $u_{\text{mp}} + fu_{\text{mp}}$ (where f is a fraction which can have any value between 0 and 1, including 0 and 1) can be determined as follows. We know that

$$u_{\text{mp}} = \sqrt{\frac{2RT}{M}}$$

$$\frac{dN_u}{N} = 4\pi\left(\frac{1}{\pi}\right)^{\frac{3}{2}} e^{-1} \times f = \frac{4f}{e\sqrt{\pi}}$$

Thus the fraction of molecules of a given range around $u_{\text{mp}}/u_{\text{avg}}/u_{\text{rms}}$ is independent of temperature, molecular mass and values of velocity. It depends upon range factor f only.

3.11 | MOLECULAR COLLISIONS

The molecular collisions can be explained based on the following postulates:

1. All molecules are identical in shape, size and there is no change in shape after collisions
2. Velocity of each molecule = u_{avg}

Let us say, that the diameter of one molecule = σ = collision diameter, then $\pi\sigma^2$ = curved surface area of an imaginary cylinder which is the collision cross-sectional area.

Consider that a single molecule is moving and other molecules are stationary. Then the moving molecule will collide with all the molecules whose center lies within distance σ from the center of the moving molecule (Fig. 3.27). Therefore, volume covered by moving molecule in unit time = volume of cylinder = $\pi\sigma^2 u_{\text{avg}}$, where u_{avg} is the distance covered per unit time

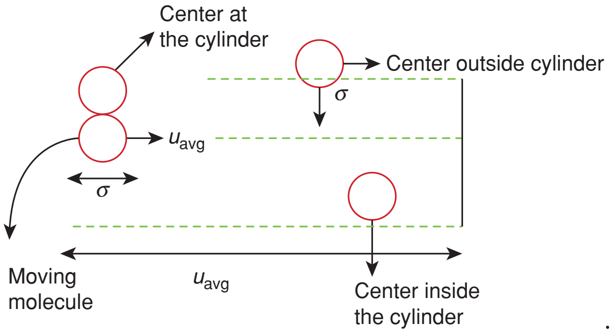


Figure 3.27 Molecular collisions.

Let N be the total number of molecules and the volume of the container be V. Then, the number of molecules per unit volume

$$N^* = \frac{N}{V}$$

Therefore, total number of molecules present in volume covered by moving molecules = $\pi\sigma^2 u_{\text{avg}} N^*$

Hence, the number of collisions made by moving molecule per unit time

$$Z_1 = \pi\sigma^2 u_{\text{avg}} N^*$$

This is based on the assumption that all other molecules are stationary. However in practice, all molecules are moving and therefore we have to consider relative velocity. On an average, molecules will collide with each other when they are moving perpendicular to each other.

$$u_{\text{rel}} = \sqrt{u_{\text{avg}}^2 + u_{\text{avg}}^2} = \sqrt{2}u_{\text{avg}}$$

Hence, the number of collisions made by a single molecule per unit time when all the molecules are moving is

$$Z_1 = \sqrt{2}\pi\sigma^2 u_{\text{avg}} N^*$$

The total number of bimolecular collisions per unit volume, per unit time

$$Z_{11} = \frac{Z_1 \times N/V}{2} = \frac{Z_1 N^*}{2}$$

$$Z_{11} = \frac{\pi\sigma^2 u_{\text{avg}} (N^*)^2}{\sqrt{2}}$$

This is the collision frequency, when each collision involves two molecules.

Note: In case of bimolecular collisions between two different molecules (Fig. 3.28), the number of molecules present in the volume are

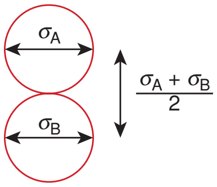


Figure 3.28 Bimolecular collisions between different molecules.

$$N_A^* = \frac{N_A}{V} \text{ and } N_B^* = \frac{N_B}{V}$$

The effective(reduced) mass

$$\mu = \sqrt{\mu_1^2 + \mu_2^2}$$

$$= \sqrt{\frac{8RT}{\pi M_1} + \frac{8RT}{\pi M_2}} = \sqrt{\frac{8RT}{\pi\mu}}$$

Total number of collisions per unit volume per unit time

$$Z_{12} = \pi\left(\frac{\sigma_A + \sigma_B}{2}\right)^2 \sqrt{\frac{8RT}{\pi\mu}} N_A^* N_B^*$$

Mean Free Path (λ)

Mean free path (λ) is the average distance travelled by a molecule between two consecutive collisions.
Distance travelled for Z_1 collisions = u_{avg}

Distance travelled for one collision $= \frac{u_{avg}}{Z_1}$

$$\lambda = \frac{u_{avg}}{Z_1} = \frac{1}{\sqrt{2}\pi\sigma^2 N^*}$$

$$\lambda = \frac{V}{\sqrt{2}\pi\sigma^2 N}$$

From ideal gas equation

$$pV = nRT$$

$$pV = \frac{N}{N_A}RT = NT\left(\frac{R}{N_A}\right) = NTk$$

where k is the Boltzmann constant. Then

$$\lambda = \frac{kT}{\sqrt{2}\pi\sigma^2 p}$$

The effect of change in physical condition on λ can be summarized as follows:

At constant p	At constant T	At constant V
$\lambda \propto T$ $\lambda \propto V$ (as $V \propto T, n$ and p are constant)	$\lambda \propto \frac{1}{p}$ $\lambda \propto V$ (as $p \propto 1/V, n$ and T are constant)	λ = constant (n is constant)

Similarly, the effect of change in physical condition on Z_{11} can be summarized as follows:

At constant p	At constant T	At constant V
$Z_{11} \propto \frac{1}{V}\sqrt{T}$ $Z_{11} \propto \frac{1}{\sqrt{V^2}}$ (as $T \propto V$) $Z_{11} \propto \frac{1}{\sqrt{T^3}}$	$Z_{11} \propto \frac{1}{V^2}$ $Z_{11} \propto p^2$ (As $p \propto 1/V$)	$Z_{11} \propto \sqrt{T}$ $Z_{11} \propto \sqrt{p}$ (as $p \propto T$)

Solved Example 3-34

The average velocity of a gas is 400 ms^{-1}, find the rms velocity of the gas. **(IIT-JEE 2003)**

Solution

The rms and average velocities are given by

$$u_{\text{rms}} = \left(\frac{3RT}{M}\right)^{1/2} \qquad u_{\text{avg}} = \left(\frac{8RT}{\pi M}\right)^{1/2}$$

Finding $u_{\text{rms}}/u_{\text{avg}}$, we get

$$\frac{u_{\text{rms}}}{u_{\text{avg}}} = \left(\frac{3RT}{M}\right)^{1/2} \times \left(\frac{\pi M}{8RT}\right)^{1/2} = \left(\frac{3\pi}{8}\right)^{1/2} = 1.085$$

Thus, $u_{\text{rms}} = 1.085 \times u_{\text{avg}} = 1.085 \times 400 = 434 \text{ m s}^{-1}$

Solved Example 3-35

The mean free path of gas A, with molecular diameter equal to 4 Å contained in a vessel, at a pressure of 10^{-6} torr is 6990 cm. The vessel is evacuated and then filled with gas B, with molecular diameter, equal to 2 Å at a pressure of 10^{-3} torr, the temperature remaining the same. What will be the mean free path of gas B?

Solution

The mean free path of gas molecules,

$$\lambda = \frac{1}{\sqrt{2}\sigma^2\left(\frac{N}{V}\right)}$$

$$\Rightarrow \lambda \propto \frac{1}{N\sigma^2} \quad \text{and} \quad \lambda \propto \frac{1}{p\sigma^2}$$

$$6990 \text{ cm} \propto \frac{1}{10^{-6} \times 4^2} \quad \text{and} \quad x \propto \frac{1}{10^{-3} \times 2^2}$$

$$\frac{6990}{x} = \frac{10^6}{16} \times 10^{-3} \times 4 = 250$$

Therefore, $x = \frac{6990}{250} = 27.96 \text{ cm} \approx 28 \text{ cm}$

Solved Example 3-36

Velocities of four gas molecules are 2, 3, –4, –1 ms^{-1}, respectively. Find out the mean velocity, mean speed, mean square velocity and root mean square velocity.

Solution

The quantities are determined as follows:

$$\text{Mean velocity} = \frac{2+3-4-1}{4} = 0$$

$$\text{Mean speed} = \frac{2+3+4+1}{4} = 2.5\ \text{ms}^{-1}$$

$$\text{Mean square velocity, } \overline{v}^2 = \frac{2^2+3^2+(-4)^2+(-1)^2}{4}$$

$$= \frac{4+9+16+1}{4} = 7.5\ \text{m}^2\text{s}^{-2}$$

$$\text{Root mean square velocity, } u_{\text{rms}} = \sqrt{\overline{u^2}} = \sqrt{7.5}$$

$$= 2.7386\ \text{ms}^{-1}$$

Solved Example 3-37

Two perfect gases at absolute temperatures T_1 and T_2 are mixed. Assuming there is no loss of energy, find the temperature of the mixture if the masses of the molecules are m_1 and m_2 and the number of molecules in the gases are n_1 and n_2.

Solution

According to the kinetic theory of gases, the kinetic energy of an ideal gas molecule at temperature T is given by K.E. = $(3/2)kT$. As there is no force of attraction among the molecules of a perfect gas, P.E. of the molecule is zero. So the energy of a molecule of perfect gas is

$$E = \text{K.E.} + \text{P.E.} = \frac{3}{2}kT + 0 = \frac{3}{2}kT$$

Now, if T is the temperature of the mixture, by conservation of energy, we have

$$n_1E_1 + n_2E_2 = (n_1+n_2)E$$

or

$$n_1\left(\frac{3}{2}kT_1\right) + n_2\left(\frac{3}{2}kT_2\right) = (n_1+n_2)\frac{3}{2}kT \Rightarrow T = \frac{(n_1T_1+n_2T_2)}{(n_1+n_2)}$$

Solved Example 3-38

Find the temperature at which methane and ethane will have the same rms speed as carbon dioxide at 400°C. Also calculate the mean velocity and most probably velocity of methane molecules at 400°C.

Solution

The rms velocity is

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

Let 1 represent CO_2 and 2 represent methane. For u_{ms} to be same for 1 and 2,

$$\frac{T_1}{M_1} = \frac{T_2}{M_2}$$

For methane and ethane the temperature is found as

$$T_{\text{methane}} = \frac{673}{44}\times 16 = 244.73\ \text{K}$$

$$T_{\text{ethane}} = \frac{673}{44}\times 30 = 458.86\ \text{K}$$

The mean speed and mean probable velocity for methane are as follows:

$$\text{Mean speed} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8\times 8.31\times 673}{3.14\times 16\times 10^{-3}}} = 943.68\ \text{ms}^{-1}$$

$$\text{Mean probable speed} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{8\times 8.31\times 673}{16\times 10^{-3}}}$$

$$= 836.11\ \text{ms}^{-1}$$

3.12 | REAL GASES AND THEIR DEVIATION FROM IDEAL GAS BEHAVIOR

The law $pV = nRT$ is called "ideal" because it follows from the assumptions of the kinetic theory, which describes an ideal gas. The molecules of an ideal gas have negligible volume and no attraction or repulsion for each other. The molecules of a "real" gas, however, have a volume, and there is some interaction between molecules, especially at high pressures (i.e., the molecules are pressed close together) and low temperatures (i.e., the molecules move more slowly).

According to the ideal gas law, the ratio pV/T equals a product of two constants, nR. But, experimentally, for real gases pV/T is actually not quite a constant. When we use experimental values of p, V and T for a real gas, such as O_2, to plot actual values of pV/T as a function of p, we get the curve shown in Fig. 3.29. The *horizontal* line at $pV/T = 1$ in Fig. 3.29 is what we should see if pV/T were truly constant over all values of p, as it would be for an ideal gas. It is observed that there is a negative deviation from ideal behavior first followed by an increase in the pV value.

In the Fig. 3.29, two types of curves are seen. The curve for dihydrogen shows an increase in pV/T values as the pressure increases and only positive deviation is seen. The plots for nitrogen, methane and carbon dioxide are similar to the plot for oxygen. The pV/T value first decreases with increase in pressure, reaches a minimum value that is characteristic of the gas and then rises. It crosses the value for an ideal gas and then shows a positive deviation from ideal gas value.

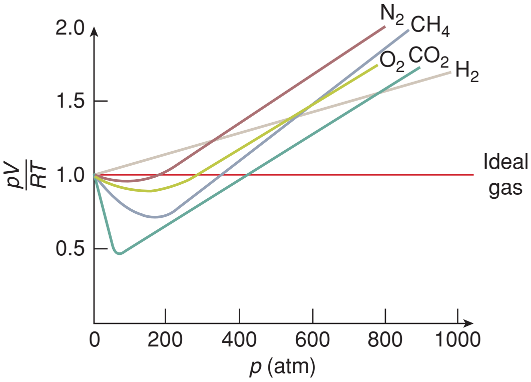


Figure 3.29 Deviation from the ideal gas law for oxygen and other gases.

The deviation in ideal gas behavior can also be seen when the pressure–volume graph is plotted for real gases, both for experimentally determined values and those calculated using Boyle's law. The measure volumes are close to the calculated values at low pressures but at high pressure conditions, the measured volume is more than the calculated volume.

It has been experimentally established that real gases do not obey ideal gas laws perfectly at all conditions of temperature and pressure. A real gas, like oxygen, deviates from ideal behavior for two important reasons:

1. The model of an ideal gas assumes that gas molecules are infinitesimally small, but real molecules do take up some space.
2. In an ideal gas, there would be no attractions between molecules, but in a real gas molecules experience weak attractions towards each other.

Deviations from ideal behavior are felt most when the gas is at very high pressure and when the temperature is low. Raising the pressure can reduce only the empty space between the molecules, not the volume of the individual particles themselves. At high pressure, the space taken by the molecules themselves is a significant part of the total volume, so doubling the pressure cannot have the total volume. As a result, the actual volume of a real gas is larger than expected for an ideal gas, and the ratio pV/T is larger than if the gas were ideal. We see this for O_2 at the right side of the graph in Fig. 3.29.

The attractive forces between molecules reveal themselves by causing the pressure of a real gas to be slightly lower than that expected for an ideal gas. The attractions cause the paths of the molecules to bend whenever they pass near each other. Because the molecules are not traveling in straight lines, as they would in an ideal gas, they have to travel farther between collisions with the walls. As a result, the molecules of a real gas do not strike the walls as frequently as they would if the gas was ideal, and this reduced frequency of collision translates to a reduced pressure. Thus, the ratio pV/T is *less* than that for an ideal gas, particularly where the problem of particle volume is least, at lower pressures. The curve for O_2 in Fig. 3.29, therefore, dips at lower pressures.

Solved Example 3-39

Why do most gases behave nearly as ideal gases at room temperature and atmospheric pressure?

Solution

Most gases behave nearly like an ideal gas, also for two reasons:

(a) The space between the molecules is so large that the volume occupied by the molecules themselves is insignificant. By doubling the pressure, we are able to squeeze the gas into very nearly half the volume.

(b) The molecules are moving so rapidly and are so far apart that the attractions between them are hardly felt. As a result, the gas behaves almost as though there are no attractions.

The van der Waals Equation for Deviations from Ideal Behavior

Many attempts have been made to modify the equation of state of an ideal gas to get an equation that better fits the experimental data for individual real gases. One of the more successful efforts was that of J. D. van der Waals. He found ways to correct the measured values of p and V to give better fits of the data to the general gas law equation. The result of his derivation is called the *van der Waals equation of state for a real gas.* Let us take a brief look at how van der Waals made corrections to measured values of p and V to obtain expressions that fit the ideal gas law.

From the ideal gas equation

$$p'V' = nRT$$

Here p' is the pressure exerted by gas molecules when there was no attractive force between the gas molecules and V' is the free volume available for motion of gas molecules.

1. **Volume correction term:** Since real gas occupies considerable volume, therefore

   Free volume = Volume of the container – effective volume occupied by gas molecules
   Let b = effective volume occupied by 1 mol of gas, then for n moles

   $V' = V - nb$

   where V is the volume of the container.
   To understand b, let us consider collision between two molecules (Fig. 3.30).

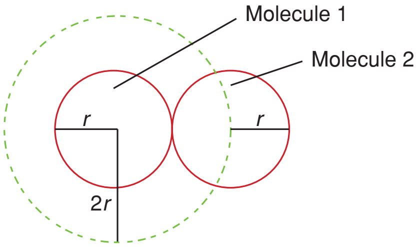


Figure 3.30 Bimolecular collision for volume correction term.

   In the frame of reference of first molecule, during collision if the second molecule is at a distance ≤ $2r$, it will collide. Therefore volume not available for this pair to freely move

$$= \frac{4}{3}\pi(2r)^3 = \frac{4}{3}\pi(8r^3)$$

   Therefore, volume unavailable for one molecule

$$= \frac{4}{3}\frac{\pi(8r^3)}{2} = 4\times\frac{4}{3}\pi r^3$$

   Then volume effectively occupied by 1 mol

$$b = 4\times\frac{4}{3}\pi r^3 \times N_A$$

   Thus volume of 1 molecule

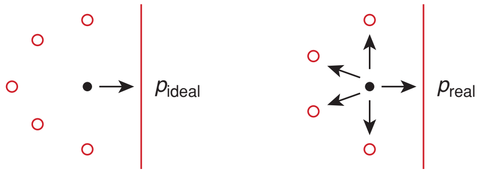
$$b \propto r^3$$

   Since b depends on the radius of the molecule, it will be different for different gases. Here b is known as van der Waal's constant.

$$[V] = [bn]$$

   Unit of b = l/mol or m^3/mol or cm^3/mol

2. **Pressure correction term:** An ideal gas has no attractive forces between the molecules whereas real gas molecules have attractive forces as shown in Fig. 3.31(a) and (b).



(a) (b)

Figure 3.31 Force of attraction between molecules in (a) ideal and (b) real gas.

Therefore, $p_{\text{ideal}} > p_{\text{real.}}$ Hence,

$$p' = p + (\text{pressure correction term})$$

Here, p' is the pressure if there is no force of attraction and p is the observed pressure of the gas. The factors affecting pressure correction terms are:

(a) Number of molecules per unit volume: More the number of molecules per unit volume, more will be the force of attraction with which molecule is pulled behind and more will be the decrement in pressure. Thus

$$p_{\text{correction}} \propto N^*$$

(b) Number of molecules striking the wall of the container: More the number of molecules striking the wall of container, more will be the pressure correction term. The number of molecules striking the wall of container depends upon number of molecules per unit volume. Thus

$$p_{\text{correction}} \propto N^*$$

Therefore, overall pressure correction term

$$p_{\text{correction}} \propto \left(\frac{n}{V}\right)^2$$

$$p_{\text{correction}} = \frac{an^2}{V^2}$$

where a is a van der Waal's constant. The value of a depends upon intermolecular force of attraction. Higher the inter-molecular force of attraction greater is overall pressure.

The van der Waal's equation for real gases is

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

For one mole of gas

$$\left(p + \frac{a}{V_{\text{m}}^2}\right)(V_{\text{m}} - b) = RT$$

Here V_{m} is the molar volume.

The van der Waals constants are determined for each real gas by carefully measuring p, V and T under varying conditions. Then trial calculations are made to figure out what values of the constants give the best matches between the observed data and the van der Waals equation. The values of van der Waals constants for a number of gases are given in Table 3.2.

Table 3.2 van der Waals constants

Gas	He	Ne	Ar	Kr	Xe	H_2	O_2	N_2	CH_4	CO_2	NH_3	H_2O	C_2H_5OH
a (L^2 atm mol^{-2})	0.03421	0.2107	1.345	2.318	4.194	0.02444	1.360	1.390	2.253	3.592	4.170	5.464	12.02
b (L mol^{-1})	0.02370	0.01709	0.03219	0.03978	0.05105	0.02661	0.03183	0.03913	0.04278	0.04267	0.03707	0.03049	0.08407

Solved Example 3-40

Calculate the pressure exerted by one mole of CO_2 gas at 273 K, if the van der Waals constant $a = 3.592$ dm^6 atm mol^{-2}. Assume that the volume occupied by CO_2 molecules is negligible. **(IIT-JEE 2000)**

Solution

The van der Waals equation for 1 mol of gas is given by

$$\left(p+\frac{a}{V^2}\right)(V-b)=RT$$

The volume occupies by CO_2 molecules is negligible implies that $b = 0$. Substituting given values and considering $V = 22.4$ L for 1 mol of gas at 1 atm, we get

$$p=\frac{RT}{V}-\frac{a}{V^2}=\frac{0.082\times 273}{22.4}-\frac{3.592}{22.4^2}$$

$$=\frac{501.45-3.592}{501.76}=\frac{497.85}{501.76}=0.9922 \text{ atm}$$

Solved Example 3-41

A graph is plotted for a real gas which follows van der Waals equation with pV_m taken on y-axis and p on x-axis. Find the intercept of the line where V_m is the molar volume. **(IIT-JEE 2004)**

Solution

For a real gas, the plot of pV_m vs. p can be of two types A or B, but at the point of intercept, that is, $p = 0$ or when p is low, van der Waals equation reduces to ideal gas equation $pV = nRT$. For 1 molar, comparing $pV_m = RT$ with $y = mx + C$, we get the intercept on y-axis as RT (Fig. 3.32).

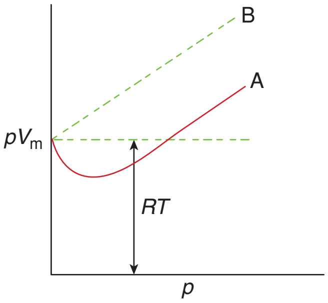


Figure 3.32

Solved Example 3-42

Calculate the pressure of one mole of nitrogen gas in a 10 L cylinder at 50°C using the van der Waals equation. Compare this value with that obtained from ideal gas equation (van der Waals constants a and b for nitrogen are 1.4 L^2 atm mol^{-2} and 0.04 L^2 mol^{-1}, respectively).

Solution

From the van der Waals equation $\left(p+\frac{a}{V^2}\right)(V-b)=RT$, we get

$$\left(p+\frac{1.4}{100}\right)(10-0.04)=0.0821\times 323 \Rightarrow p=2.648 \text{ atm}$$

From ideal gas equation, we have

$$p=\frac{RT}{V}=\frac{0.0821\times 323}{10}=2.652 \text{ atm}$$

Solved Example 3-43

Calculate the pressure exerted by 5 mol of CO_2 in 1 L vessel at 47°C using van der Waals equation. Also, calculate the pressure for an ideal gas. Given $a = 3.592$ atm L^{2}mol^{-2}, $b = 0.0427$ L mol^{-1}

Solution

From the van der Waals equation, we have

$$\left(p+\frac{an}{V^2}\right)(V-nb)=nRT$$

Substituting $n = 5$, $V = 1$ L, $T = 320$ K, $a = 3.592$ atm L^2 mol^{-2} and $b = 0.0427$ mol^{-1}, we get

$$p = \frac{nRT}{(V - nb)} - \frac{an^2}{V^2} = \frac{5 \times 0.082 \times 320}{1 - 5 \times 0.0427} - \frac{3.592 \times 25}{1}$$
$$= 166.81 - 89.8 = 77.01 \text{ atm}$$

For an ideal gas, we have

$$p = \frac{nRT}{V} = \frac{5 \times 0.082 \times 320}{1} = 131.2 \text{ atm}$$

3.13 | COMPRESSIBILITY FACTOR

At low temperatures, the intermolecular attractive interactions increase because the average kinetic energy; and hence the speed of molecules decreases. The intermolecular repulsive interactions increase at high pressure. The real gas molecules will show ideal gas behavior when the intermolecular interactions are negligible, that is, when pressure approaches zero.

The ratio of the observed volume of a gas to the calculated volume under given conditions of temperature and pressure is known as **compressibility factor (Z)** of the gas. If the observed volume of a gas at pressure p and temperature T is V_{real} and the calculated volume from ideal gas equation V_{ideal} is nRT/p, then the compressibility factor is

$$Z = \frac{V_{\text{real}}}{nRT/p} = \frac{pV_{\text{real}}}{nRT} \Rightarrow Z = \frac{V_{\text{real}}}{V_{\text{ideal}}} \qquad (3.48)$$

For an ideal gas, $Z = 1$ as $pV = nRT$ and for a real gas $Z \neq 1$, so the observed volume is either greater or less than the calculated volume.

The temperature at which gases show ideal gas behavior for an appreciable range of pressure is known as **Boyle's temperature** or **point**. It is specific to the nature of the gas. At this temperature the rate of change of pV approaches zero (i.e., remains constant). It is therefore, given by

$$T_{\text{Boyle}} = \frac{\partial pV}{\partial R} = \frac{a}{Rb} = \frac{1}{2T_{\text{inv}}} \qquad (3.49)$$

where a and b are van der Waals constants and T_{inv} is the inversion temperature.

As the temperature increases beyond the Boyle's point, the forces of attraction between gas molecules become weak and gases show positive deviation from ideality ($Z > 1$). Below the Boyle's point, the gases first show a negative deviation from ideality, reach a minimum value with increasing value of pressure and then show positive deviation ($Z > 1$) continuously.

For an ideal gas the plot of Z vs. p is a straight line parallel to the pressure axis (Fig. 3.33). As the pressure is varied, Z for real gases deviates from unity.

For 1 mole, van der Waals equation is $\left(p + \frac{a}{V_{\text{m}}^2}\right)(V_{\text{m}} - b) = RT$

Case 1: At low pressure, $V_{\text{m}} - b \approx V_{\text{m}}$, therefore, $\left(p + \frac{a}{V_{\text{m}}^2}\right)(V_{\text{m}} - b) = RT$ becomes

$$pV_{\text{m}} + \frac{a}{V_{\text{m}}} = RT$$

or

$$\frac{pV_{\text{m}}}{RT} + \frac{a}{V_{\text{m}}RT} = \frac{RT}{RT}$$

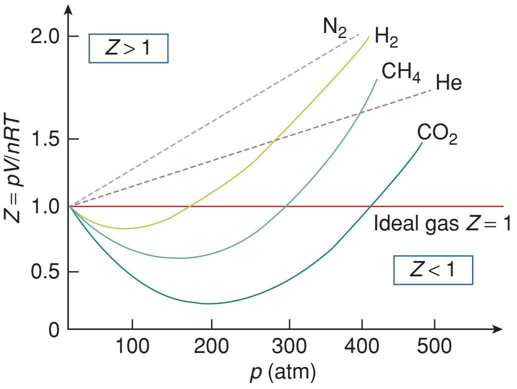


Figure 3.33 Variation in compressibility factor of some gases.

Therefore,
$$Z = 1 - \frac{a}{V_m RT} \tag{3.50}$$

This indicates that $Z < 1$ at low pressure region, the gas is more compressible and attractive forces dominate.

Case 2: At high pressure, $p + \frac{a}{V_m^2} \approx p$. Therefore, $pV_m - pb = RT$. Therefore,

$$\frac{pV_m}{RT} = \frac{RT}{RT} + \frac{pb}{RT}$$

Therefore,
$$Z = 1 + \frac{pb}{RT} \tag{3.51}$$

This indicates $Z > 1$, so repulsive forces dominate.

Note: If $Z = 1$, the repulsive and attractive forces are negligible and compensate for each other. If $Z > 1$, repulsive forces dominate attractive forces and it is difficult to compress the gas. If $Z < 1$, attractive forces dominate repulsive forces and gases are easily compressible.

The above observations can be summarized as

1. At very low pressures, all gases have Z close to unity. At low pressures, the volume of gas is large, so the volume of the gas molecules can be neglected and gases can behave as ideal gases.
2. As the pressure increases, the value of pV/nRT first decreases ($Z < 1$), reaches a minimum value and then increases.
3. At high pressures $Z > 1$, so the gases become difficult to compress as the pressure increases.

Note: Hydrogen (and also helium) show exceptional behavior. The compressibility factor of hydrogen gas at 273 K increases with increase in pressure and has $Z > 1$ at all pressures. This is because the kinetic energy of molecules at 273 K is very large and the attractive interactions are insignificant. The increase in pressure reduces the molecular separation, the repulsive interactions become predominant and gas shows positive deviation from ideality. Negative deviations can be observed at temperatures much lower than 273 K.

We have seen that the behavior of gases becomes close to ideal gases at low pressure. However, up to what pressure the gas will exhibit ideal gas behavior will depend on the nature of the gas and the temperature at which the study is conducted.

Virial Equation

Various equations have been developed for real gases based on the different pressure, volume and temperature values. These equations are called equations of state, as these represent the state properties of the substance at equilibrium. The equation of state in terms of compressibility factor is called the **virial equation**.

$$Z = \frac{pV_m}{RT} = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \frac{D}{V_m^2} + \ldots \tag{3.52}$$

It is derived as follows

$$Z = \left(1 - \frac{b}{V_m}\right)^{-1} - \frac{a}{V_m RT}$$

Here
$$\left(1 - \frac{b}{V_m}\right)^{-1} = 1 + \frac{b}{V_m} + \left(\frac{b}{V_m}\right)^2 + \left(\frac{b}{V_m}\right)^3 + \ldots.$$

Therefore,
$$Z = 1 + \left(b - \frac{a}{RT}\right) \times \frac{1}{V_m} + (b^2)\left(\frac{1}{V_m^2}\right) + \ldots.$$

Here, we get Eq. (3.52), if
$$B = b - \frac{a}{RT},\ C = b^2,\ D = b^3$$

The virial equation is a power series expansion in variable V. The coefficients $B, C \ldots$ are functions of temperature and are called first virial coefficient, second virial coefficient and so on. These are substance and temperature specific.

Reduction of van der Waals Equation to Virial Equation

The expression of van der Waals equation for one mole of gas is

$$\left(p + \frac{a}{V_m^2}\right)(V_m - b) = RT$$

or
$$p = \frac{RT}{(V_m - b)} - \frac{a}{V_m^2}$$

Multiplying this equation by V_m/RT, we get

$$\frac{pV_m}{RT} = \frac{V_m}{V_m - b} - \frac{a}{V_m RT}$$

$$Z = \left(1 - \frac{b}{V_m}\right)^{-1} - \frac{a}{V_m RT}$$

$$\left(1 - \frac{b}{V_m}\right)^{-1} = 1 + \frac{b}{V_m} + \left(\frac{b}{V_m}\right)^2 + \left(\frac{b}{V_m}\right)^3 + \ldots$$

Therefore,

$$Z = 1 + \left(\frac{b - a}{RT}\right) \times \frac{1}{V_m} + \left(\frac{b}{V_m}\right)^2 + \left(\frac{b}{V_m}\right)^3 + \ldots \quad (3.53)$$

Comparing Eq. (3.52) with Eq. (3.53), we get the second virial coefficient, $B = \dfrac{b - a}{RT}$ and similarly for third coefficient, $C = b^2$.

Solved Example 3-44

The compression factor (compressibility factor) for one mole of a van der Waals gas at 0°C and 100 atm pressure is found to be 0.5. Assuming that the volume of a gas molecule is negligible, calculate the van der Waals constant a.

(IIT-JEE 2001)

Solution

The compressibility factor is given by $Z = pV/nRT$. Therefore, substituting values, we get the volume as

$$V = \frac{Z \times n \times R \times T}{p} = \frac{0.5 \times 1 \times 0.082 \times 273}{100} = 0.111\ \text{L}$$

When the volume of the gas is negligible, the van der Waals constant $b = 0$, so the equation becomes

$$pV = RT - \frac{a}{V}$$

$$a = RTV - pV^2 = 0.082 \times 273 \times 0.111 - 100(0.111)^2$$
$$= 2.48 - 1.23 = 1.25\ \text{atm L}^2\ \text{mol}^{-2}$$

Solved Example 3-45

Starting from the van der Waals equation of state show that the Boyle's temperature, $T_B = a/Rb$.

Solution

The van der Waals equation $\left(p+\frac{an}{V^2}\right)(V-nb)=nRT$ can be written as

$$pV+\frac{a}{V}+pb-\frac{ab}{V^2}=RT$$

At the Boyle's temperature T_B, the volume of the gas is appreciably large, therefore we can neglect the term ab/V^2 for its lower value. Hence, the equation becomes

$$pV+\frac{a}{V}-pb=RT$$

or
$$\left[\frac{\partial(pV)}{\partial p}\right]_{T_B}-\frac{a}{V^2}\left(\frac{\partial V}{\partial p}\right)_{T_B}-b=0$$

At the Boyle's temperature T_B, $\left[\frac{\partial(pV)}{\partial p}\right]_{T_B}=0$ because pV is independent of p. Therefore,

$$-\frac{a}{V^2}\left(\frac{\partial V}{\partial p}\right)_{T_B}-b=0 \qquad (1)$$

Now at Boyle's temperature, the given gas will follow the ideal gas equation

$$pV=RT_B \Rightarrow V=\frac{RT_B}{p}$$

Differentiating with respect to p, we get

$$\left(\frac{\partial V}{\partial p}\right)_{T_B}=\frac{-RT_B}{p^2}=\frac{-RT_B}{R^2T_B^2/V^2}=\frac{-V^2}{RT_B}$$

Putting the value of $\left(\frac{\partial V}{\partial p}\right)_{T_B}$ in Eq. (1), we get

$$\frac{a}{RT_B}-b=0 \Rightarrow \frac{a}{RT_B}=b \Rightarrow T_B=\frac{a}{Rb}$$

At this temperature, the gas behaves as an ideal gas since $Z = 1$.

Solved Example 3-46

The compressibility factor is always greater than 1 and increases with increase of pressure for hydrogen and helium. Explain.

Solution

The intermolecular forces of attraction in hydrogen and helium are negligible as they are small molecules, that is, the van der Waals constant "a" is very very small so that a/V^2 is negligible. The van der Waals equation, therefore, becomes

$$p(V-b)=RT \Rightarrow pV=RT+pb$$

Dividing by RT throughout, we get

$$\frac{pV}{RT}=1+\frac{pb}{RT}$$

Now, $Z = pV/RT$ which is greater than 1, and increases with increase in the value of p at constant T.

Solved Example 3-47

Assuming CO_2 to be van der Waals gas, calculate its Boyle temperature. Given a = 3.59 atm L^2 mol^{-2}; b = 0.0427 L mol^{-1}.

Solution

Boyle temperature in terms of van der Waals constants is:

$$T_B=\frac{a}{Rb}$$

Hence,

$$T_B=\frac{3.59\ \text{atm L}^2\text{mol}^{-2}}{(0.0821\ \text{L atm K}^{-1}\ \text{mol}^{-1})(0.0427\ \text{L mol}^{-1})}=1024\ \text{K}$$

Solved Example 3-48

A mole of CCl_4 vapors at 77°C occupies a volume of 36.0 L. If van der Waals constants are a = 20.39 L^2 atm mol^{-2} and b = 0.1383 L mol^{-1}, calculate the compressibility factor Z under **(a)** low pressure region and **(b)** high pressure region.

Solution

(a) Under low pressure region, the molar volume is high, so $V_m - b \approx V_m$. The following equation

$$\left(p + \frac{a}{V_m^2}\right)(V_m - b) = RT$$

then becomes $\quad pV_m + \dfrac{a}{V_m} = RT$

So, the compressibility factor is

$$Z = 1 - \frac{a}{RTV_m} = 1 - \frac{20.39}{0.0821 \times 350 \times 35} = 0.98$$

(b) Under high pressure p is high, so $p + \dfrac{a}{V_m^2} \approx p$. Substituting, we get

$$p(V_m - b) = RT \Rightarrow p = \frac{RT}{V_m - b}$$

Now, the compressibility factor is

$$Z = \frac{pV_m}{RT} = \frac{V_m}{V_m - b} = \frac{1}{1 - (b/V_m)} = \frac{1}{1 - (0.138/35)} = 1.004$$

3.14 | LIQUEFACTION OF GASES

Thomas Andrews plotted isotherms of carbon dioxide at various temperatures and was the first to obtain complete data on the variation of three variables – pressure, volume and temperature, in both gaseous and liquid state (Fig. 3.34). He observed that at high temperatures, the isotherms looked like those for an ideal gas and the gas cannot be liquefied even at very high pressure. At lower temperatures, the isotherms show a considerable variation from ideal gas behavior. The liquid carbon dioxide first makes appearance in the isotherm at 30.98°C at 73 atm pressure. This temperature is known as the critical temperature (***T***$_C$) and the pressure is known as critical pressure (***p***$_C$) of carbon dioxide and the volume of one mole of gas under these conditions is known as critical volume (***V***$_C$). These are collectively known as **critical constants** of the gas. The isotherm corresponding to critical temperature is critical isotherm and the substance exists in liquid and gaseous state on either side of it.

Based on the isotherms for carbon dioxide, the following important observations can be made about the liquid–gas equilibrium in carbon dioxide.

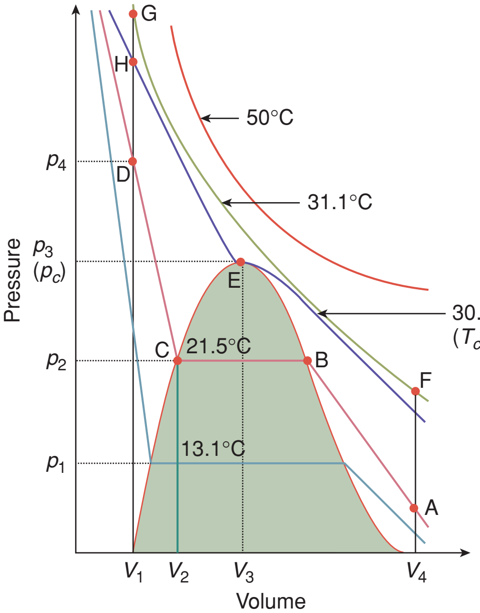


Figure 3.34 Isotherms of carbon dioxide at various temperatures.

1. On increase in the pressure beyond the critical pressure, the curve obtained represents only the compressibility of the liquid, and the steep curve beyond 73 atm represents the isotherm of the liquid. A slight decrease in volume (compression) results in considerable increase in pressure.
2. Below the critical temperature (30.98°C), the gas shows different behavior on compression.
3. At temperature of 21.5°C, carbon dioxide exists as a gas up to point B beyond which a liquid of certain volume is obtained.
4. Further decrease in volume does not affect the pressure up to point C, as indicated by the straight line BC. Further compression only condenses more gas into liquid and the liquid and gaseous carbon dioxide coexist. At point C, all the gas is compressed to a liquid and further increase in pressure causes compression of the liquid as shown by the steep curve CD. A small decrease in volume from V_2 to V_3 results in sharp increase in pressure from p_2 to p_3.
5. All the isotherms below the critical temperature show a similar pattern, the difference being only in the length of straight line BC. The length of the straight line converges into a point at E, which corresponds to the critical temperature.

6. In the isotherm plots, regions of pure gaseous state and pure liquid state are indicated by points such as A and D, respectively. The coexistence of gaseous and liquid states is represented by the shades in the area under the curve.
7. In the graph, the gas can be moved from point A to F by increasing the temperature and then compressed to point G by increasing the pressure at constant temperature, along the isotherm at temperature 31.1°C. On lowering the temperature, we can vertically move down to point D, crossing the critical isotherm at point H. So, carbon dioxide exists as a liquid here and we have crossed over from gaseous to liquid state without passing a stage where these states coexist. Hence, for a phase transition carried out below the critical temperature, substance always exists in a single phase.

All gases on compression at constant temperature show similar behavior as shown by carbon dioxide. From the characteristic features of the isotherms for carbon dioxide, we can conclude the following for all gases:

1. The critical temperature of the gas is the highest temperature at which liquefaction of gases first occurs.
2. In case of permanent gases, that is, gases which show positive deviation from ideal gas behavior, the liquefaction requires cooling as well as compression. On cooling and compression, the gas molecules move close together, the intermolecular forces increase and gases liquefy.
3. There is continuity in the liquid and gaseous states and the term fluid is used to represent the continuity in both the states.
4. The two phases can be distinguished when they are above or below the critical temperature. At critical temperature, the liquid passes into the gas phase continuously and the boundary between the two phases disappears.
5. A gas below the critical temperature can be liquefied by applying pressure and is known as **vapor** of the substance.

Expressions of Critical Constants in Terms of van der Waals Constants

For one mole of gas, the van der Waals equation, $\left(p+\dfrac{a}{V_m^2}\right)(V_m-b)=RT$

can be written as
$$V_m^3-\left(b+\frac{RT}{p}\right)V_m^2+\frac{a}{pV_m}-\frac{ab}{p}=0$$

At critical point, $(V_m - V_C)^3 = 0$. Therefore,
$$3V_C = b+\frac{RT_C}{p_C}$$

Now,
$$3V_C^2=\frac{a}{p_C} \quad \text{and} \quad V_C^3=\frac{ab}{p_C}$$

$$V_C = 3b,\ p_C=\frac{a}{27b^2},\ T_C=\frac{8a}{27R_b} \tag{3.54}$$

where V_C, p_C and T_C are critical volume, critical pressure and critical temperature, respectively. Critical temperatures and pressures of some common substances are given in Table 3.3.

Table 3.3 Critical temperature and pressure of some common substances

Gas	Ar	NH_3	C_6H_6	CO_2	C_2H_5OH	He	H_2	N_2	O_2	H_2O
Critical Temperature (T_C) in K	87	405.5	561.9	304.1	516	5.3	33.2	126	154.2	647.4
Critical Pressure (p_C) in atm	6.3	111.53	47.9	73	63	2.26	12.80	33.5	49.74	0.044

Experimental Methods for Liquefaction of Gases

From studies on liquefaction of carbon dioxide, it was observed that for liquefaction of gases they need to be first cooled below their critical temperature and then pressure needs to be applied. The cooling of gases to low temperatures for their liquefaction can be achieved by any of the following methods:

1. **Adiabatic expansion:** In this method the gas is allowed to expand adiabatically against pressure. In process it does some mechanical work at the expense of kinetic energy thereby causing the temperature to fall.
2. **Rapid evaporation of a volatile liquid:** In this method any easily volatile liquid is allowed to evaporate to cool and liquefy a gas.
3. **Joule-Thomson effect:** In this effect, when a compressed gas is allowed to expand into a low pressure under adiabatic conditions, lowering of temperature is observed. The gas molecules do work at the cost of kinetic energy to overcome the intermolecular forces, which causes cooling to occur. The relation is given by:

$$\mu = \left(\frac{\partial T}{\partial p}\right)_H \tag{3.55}$$

The pressure at which gases neither cool nor warm up on expansion, that is, $\mu = 0$ is called the **inversion point**. This point varies with temperature and for a given pressure, the temperature at which a gas on passage from higher to lower pressure through fine orifice does not undergo heating or cooling ($m = 0$) is known as **inversion temperature**. At constant pressure, each gas shows two inversion temperatures, the upper and lower one, between which it undergoes cooling on expansion and beyond which it undergoes heating. Most of the gases are below their upper inversion temperature at room temperature, and hence, cool on expansion. This temperature is related to the van der Waals constants by the relation:

$$T_{\text{inv}} = \frac{2a}{Rb} \tag{3.56}$$

Joule Thomson Effect

During adiabatic free expansion of an ideal gas,

$$p_{\text{ext}} = 0, w = p\Delta V = 0$$
$$\Delta U = 0 \text{ (as } q = 0)$$

Therefore, during adiabatic free expansion of real gas, w, q and $\Delta U = 0$.

But temperature of the system changes as work is done internally against forces. ΔT may be positive or negative so we must define a temperature known as **inversion temperature** above and below which ΔT will have opposite signs, that is at $T = T_i$, $\Delta T = 0$.

If $T > T_i$, repulsive forces dominate, therefore, temperature increases or we observe a heating effect. Work done by the gas molecules is negative as gas has a tendency to expand.

If $T < T_i$, attractive forces dominate, therefore, temperature decreases or we observe a cooling effect. Work has to be done against attractive forces so that expansion takes place.

When $T = T_i$, both forces compensate each other or temperature remains constant.

Experimentally

$$T_i = 2T_b = \frac{2a}{Rb}$$

Here, T_i is the inversion temperature and T_b is Boyle's temperature.

Solved Example 3-49

The critical temperature of ammonia and hydrogen are 405.5 K and 33.2 K, respectively. Ammonia can be liquefied at room temperature just by compression of the gas at a high pressure. Liquefaction of hydrogen, on the other hand, requires cooling as well as compression. Explain.

Solution

The critical temperature of ammonia (405.5 K) is well above the room temperature, so the gas at room temperature when compressed will liquefy. The critical temperature of hydrogen (33.2 K) on the other hand is much below the room temperature, so the gas needs to be cooled and then compressed for liquefaction.

Solved Example 3-50

The van der Waals constants for gases A, B and C are as follows:

Gas	a (dm^6 kPa mol^{-2})	b (dm^3 mol^{-1})
A	405.3	0.027
B	1215.9	0.030
C	607.95	0.032

which gas has **(a)** highest critical temperature, **(b)** the largest molecular volume and **(c)** the most ideal behavior around STP?

Solution

For the critical temperature $T_C = 8a/27R_b$. Since R is constant, higher the value of a/b higher will be critical temperature.

As $V_C = 3b$ and $V_C \propto V_m$ (for a particular gas), so higher the value of V_C, higher will be molar volume of the gas. If the critical temperature is close to 273 K, gas will behave ideally around the STP.

Gas	a (dm^6 kPa mol^{-2})	b (dm^3 mol^{-1})	T_C	V_C	a/b
A	405.3	0.027	534.97 K	0.081	$1.501 \times \Delta 0^4$
B	1215.9	0.030	1444.42 K	0.09	$4.053 \times \Delta 0^4$
C	607.95	0.032	677.07 K	0.096	$1.89 \times \Delta 0^4$

(a) B gas has the largest critical temperature as T_C = 1444.42 K.

(b) C gas has the largest molecular volume as $V_C = 3b$.

(c) A gas has the most ideal behavior around STP.

Solved Example 3-51

The critical volume of a gas is 0.072 L mol^{-1}. What will be the radius of the molecule in cm?

Solution

(a) We know that $V_C = 3b$, assuming the gas to obey van der Waals equation. Therefore,

$$b = \frac{0.072}{3} = 0.024 \text{ L mol}^{-1}$$

Now,

$$b = \frac{24 \text{ cm}^3}{6 \times 10^{23}} \text{ per molecule} = 4 \times 10^{-23} \text{ cm}^3 \text{per molecule}$$

$$4 \times 10^{-23} \text{ cm}^3 \text{per molecule} = 4 \times \frac{4}{3}\pi r^3$$

$$r^3 = \frac{3}{4\pi} \times 10^{-23}$$

or

$$r = \left(\frac{3}{4\pi} \times 10^{-23}\right)^{1/3} \text{ cm}$$

$$= 1.336 \times 10^{-8} \text{ cm}$$

Solved Example 3-52

If Boyle's temperature is 25 °C, then at 100 °C gas shows which effect?

Solution

Given that $T_b = 25\ °\text{C} = 298$ K, then

$T_i = 2T_b = 596 \text{ K} = 323\ °\text{C}$

So $T = 100\ °\text{C} < T_i = 323\ °\text{C}$. Therefore, cooling effect is observed.

3.15 | LAW OF CORRESPONDING STATES

We define the following terms:

1. Reduced temperature

$$T_R = \frac{T}{T_C}$$

Here T_C is the critical temperature. Therefore

$$T = \frac{8a}{27bR} T_R$$

2. Reduced volume

$$V_R = \frac{V_m}{V_C}$$

Therefore,

$$V_m = V_R V_C$$
$$V_m = 3bV_R$$

3. Reduced pressure

$$p_R = \frac{p}{p_C}$$
$$p = p_R p_C$$
$$p = \frac{a}{27b^2} p_R$$

The van der Waal's equation is given by

$$\left(p + \frac{a}{V_m^2}\right)(V_m - b) = RT$$

Substituting for p, V_m, T from expressions for reduced terms, we have

$$\left(\frac{1}{27b^2} p_R + \frac{a}{9b^2 V_R^2}\right)(3bV_R - b) = R\left(\frac{8a}{27bR}\right) T_R$$

$$(p_R V_R^2 + 3)(3V_R - 1) = 8T_R V_R^2$$

This is the **reduced van der Waal's equation**.

3.16 | HEAT CAPACITY AND SPECIFIC HEATS OF GASES

The heat capacity (C) of a system refers to its capacity to absorb and store heat. Knowing the heat capacity of a substance, we can calculate the heat supplied to the system by monitoring the rise in temperature. If the heat capacity of a substance is large, the temperature would rise to a very small extent, as in case of water.

The molar heat capacity (C_m) is the amount of heat required to raise the temperature of one mole of the substance by 1°C (or K). Specific heat or specific heat capacity can be defined as the heat required to raise the temperature of a unit mass by 1°C (or K), at a specified temperature. The amount of heat required to bring about a temperature change (ΔT) in mass m of a substance with specific heat c, can be obtained by the relation

$$c = \frac{q}{m \times \Delta T} \tag{3.57}$$

The heat capacity of gases can be measured at constant pressure (C_p) and constant volume (C_V).

Heat Capacity at Constant Volume

It is the heat supplied to increase the temperature through 1°C at constant volume. From kinetic theory of gases, we know that kinetic energy of gas molecules is given by

$$pV = \frac{1}{3} mnu^2 = \frac{2}{3}\text{K.E.} = \frac{3}{2} RT \text{ for 1 mol of the gas}$$

When the temperature is raised by 1°C, the increase in kinetic energy is

$$\frac{3}{2}R(T+1)-\frac{3}{2}RT=\frac{3}{2}R$$

This increase is equal to the heat supplied at constant volume to raise the temperature by 1°C, so by definition

$$C_V=\frac{3}{2}R \tag{3.58}$$

This relation holds for monoatomic gases and for di- or polyatomic gases, the relation is modified to include contribution from rotational and vibration energy to the total kinetic energy, so

$$C_V=\frac{3}{2}R+x$$

Where x varies from gas to gas is zero for monoatomic gases.

Heat Capacity at Constant Pressure

It is defined at the heat supplied to one mole of the substance to increase its temperature through 1°C at constant pressure. When heat is supplied at constant pressure, it will be used to increase the kinetic energy and do pressure-volume work. We have seen that increase in kinetic energy is

$$\frac{3}{2}R+x \quad \text{or} \quad \frac{3}{2}R \quad \text{(for monoatomic gas)}$$

The pressure–volume work done by one mole of gas is given by $pV=nRT$. When the temperature changes from T to $T+1$ and the volume changes by ΔV at constant pressure, work done is given by

$$p(V+\Delta V)=R(T+1)$$

Subtracting the above equation from $pV=nRT$, we get

$$p\Delta V=R$$

So. the total energy given to the monoatomic gas is by definition the heat capacity at constant volume

$$C_p=\frac{3}{2}R+R=\frac{5}{2}R$$

The relation between the two heat capacities is given by

$$C_p=C_V+R \tag{3.59}$$

The ratio between heat capacities at constant pressure and volume is given by γ. The ratio for different gases is

$$\begin{aligned}\frac{C_p}{C_V}&=\gamma=1.66 \text{ (for monoatomic gas)}\\&=1.40 \text{ (for diatomic gas)}\\&=1.33 \text{ (for triatomic gas)}\end{aligned} \tag{3.60}$$

Solved Example 3-53

For He molecule C_V value is 3/2 R, independent of temperature. But for H_2 at very low temperature 3/2 R, at moderate temperature 5/2 R at higher temperature > 5/2 R. Explain the temperature dependence and justify.

(IIT-JEE 2003)

Solution

Helium is monoatomic, so it has only translational degrees of freedom. The contribution of translational degree of freedom towards C_V is $R/2$ so, $C_V = 3 \times R/2 = 3R/2$. On the other hand, hydrogen molecule is diatomic. At low temperature, its rotational and vibrational contribution is zero, so $C_V = 3R/2$ (same as that of He molecule). At moderate temperature, rotational contribution comes into account (i.e., $C = 2 \times R/2$) and at even higher temperature, vibrational contribution ($1 \times R$) also becomes significant.

3.17 | LIQUID STATE

The common properties of liquids are as follows:

1. They have high density. Liquids are about 1000 times denser than a typical gas because there is little empty space between the molecules as the intermolecular force of attraction is higher than in gases.
2. They are essentially incompressible. Unlike the behavior of a gas, an increase in pressure on a liquid does not result in a significant decrease in volume.
3. They undergo little thermal expansion. The degree of expansion varies for different liquids.
4. They have a fixed volume but no definite shape. Liquids flow and thus do not have a definite shape. (It is determined by the shape of the container.) But they have a fixed volume.
5. There exist considerable forces of attraction between the molecules of the liquids.
6. The molecules in liquids move randomly and like in the gases the average kinetic energy of molecules in a sample of liquid are proportional to the absolute temperature.
7. The diffusion between liquid molecules is much slower than that observed for gases because the molecules are much closely spaced in liquids than in solids. This means higher frequency of collision and less free path and hence less diffusion.
8. The densities of a substance in liquid state is much higher than the density of the same substance in the gaseous state. This again arises due to close packing of the molecules.
9. Liquids show a tendency to evaporate and hence possess vapor pressure.

Vapor Pressure

When a liquid evaporates, the molecules that enter the vapor exert a pressure called the **vapor pressure**. From the very moment a liquid begins to evaporate into the vapor space above it, there is a vapor pressure. If the evaporation is taking place inside a sealed container, this pressure grows until finally equilibrium is reached. Once the rates of evaporation and condensation become equal, the concentration of molecules in the vapor remains constant and the vapor exerts a constant pressure. This final pressure is called the **equilibrium vapor pressure or saturated vapor pressure of the liquid**. In general, when we refer to the *vapor pressure*, we really mean the equilibrium vapor pressure. The temperature should also be given when discussing vapor pressure as the process is temperature dependent.

Figure 3.35 shows plots of equilibrium vapor pressure vs. temperature for a few liquids. From these graphs, we see that both a liquid's temperature and its chemical composition are the major factors affecting its vapor pressure. Once we have selected a particular liquid, however, only the temperature matters. The reason is that the vapor pressure of a given liquid is a function solely of its rate of evaporation *per unit area of the liquid's surface*. The vapor pressure is relatively high when the evaporation rate is high. As the temperature of a given liquid increases, so does its rate of evaporation and so does its equilibrium vapor pressure.

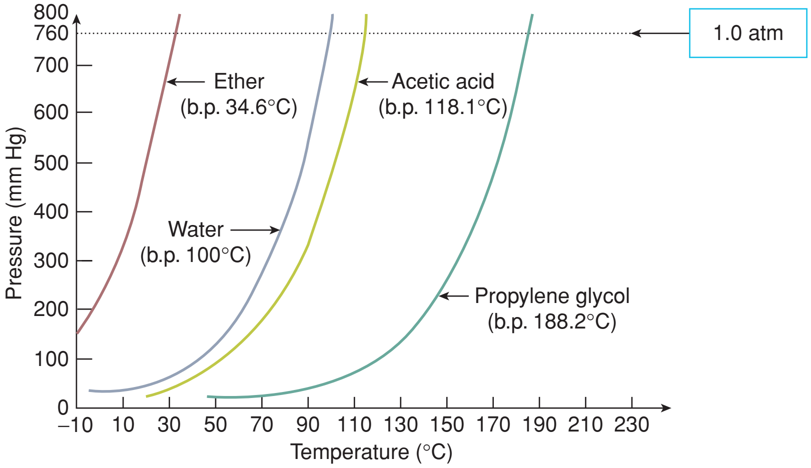


Figure 3.35 Variation of vapor pressure with temperature for some common liquids.

As chemical composition changes in going from one liquid to another, the strengths of intermolecular attractions change. If the attractions increase, the rates of evaporation at a given temperature decrease, and the vapor pressures decrease. These data on relative vapor pressures tell us that, of the four liquids in Fig. 3.35, intermolecular attractions are strongest in propylene glycol, next strongest in acetic acid, third strongest in water, and weakest in ether. Thus, we can use vapor pressures as indications of relative strengths of the attractive forces in liquids.

Factors Affecting Vapor Pressure

The magnitude of vapor pressure does not depend on the **total** surface area of the liquid nor on the volume of the liquid in the container, nor on the volume of the container itself, just as long as some liquid remains when equilibrium is reached. The reason is because none of these factors affects the rate of evaporation per unit surface area.

Increasing the *total* surface area does increase the *total* rate of evaporation, but the larger area is also available for condensation; so the rate at which molecules return to the liquid also increases. The rates of both evaporation and condensation are thus affected equally, and no change occurs to the equilibrium vapor pressure. Adding more liquid to the container cannot affect the equilibrium either because evaporation occurs from the *surface*. Having more molecules in the bulk of the liquid does not change what is going on at the surface.

The factors affecting vapor pressure are listed as follows:

1. **Temperature:** On increasing temperature, the vapor pressure increases.
2. **Nature of liquids:** Different liquids have different vapor pressures depending on their intermolecular attractive forces. Those having higher magnitude of intermolecular attractive forces have lower vapor pressure.
3. **Addition of non-volatile solute:** According to Raoult's law, the addition of a non-volatile solute lowers the vapor pressure.
4. **Weight of the substance:** Substances having lower molecular weights have higher vapor pressure.

Boiling and Melting Points

When a liquid is heated, it eventually reaches a temperature at which the vapor pressure is large enough that bubbles of vapor form inside the body of the liquid. This temperature is called the **boiling point**. A liquid boils when the pressure of the vapor escaping from the liquid is equal to the pressure exerted on the liquid by its surroundings. On heating, some liquid molecules get converted into gaseous bubbles. The vapor in the bubble is in equilibrium with the liquid. If the external vapor pressure is more than the gaseous pressure in the bubble, it collapses. However, if the vapor pressure of the bubble is more than the external pressure, it would rise to the surface and finally escape into vapor state.

The boiling point depends on the restraining pressure. The normal boiling point of a liquid is the temperature at which the vapor pressure is equal to 1 atm. The standard boiling point of a liquid is the temperature at which the vapor pressure is equal to 1 bar. The normal boiling point of water is 100°C because this is the temperature at which the vapor pressure of water is 760 mm Hg, or 1 atm. At 10,000 ft above sea level, the pressure of the atmosphere is only 526 mm Hg. At that elevation, water boils when its vapor pressure is 526 mm Hg. Water needs to be heated to only 90°C for its vapor pressure to reach 526 mm Hg.

Note: When a liquid is heated in a closed container, it does not boil. On heating, the liquid starts getting converted into vapor and the two phases are distinctly visible. As the temperature is increased further, the density of the vapor phase increases and becomes more than that of the liquid phase. As more and more liquid is converted into the vapor, the liquid phase expands and the boundaries of liquid and vapor phases merge. The temperature at which this happens is known as the **critical temperature**.

The change in state of a substance involves addition or removal of energy in the form of heat. For example, water is known to exist in all three states. The heat required to convert water to its vapor is 40.7 kJ per mole. This heat change accompanying the conversion of a liquid to its vapor is called **heat of vaporization (ΔH_{vap})**. Similarly ice can be melted into water when heat energy of 60.1 kJ per mole is supplied. This heat change when a solid is melted into a liquid is known as **heat of fusion (ΔH_{fus})**.

Clausius–Clapeyron Equation

We have seen that the vapor pressure varies with change in temperature. The variation of vapor pressure with temperature is studied using Clausius-Clapeyron equation according to which

$$\log p = \frac{-\Delta H_{\text{vap}}}{2.303RT} + A$$

where A is a constant, R is molar gas constant and a graph between log p and $1/T$ is a straight line with a negative slope $= -(\Delta H_{\text{vap}})/2.303\text{R}$.

This equation can be used to compare the vapor pressure of a liquid at two different pressures in the form:

$$\log \frac{p_2}{p_1} = \frac{\Delta H}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{3.61}$$

Vapor Pressure of Solids

Certain volatile solids evaporate readily and convert into vapors by the process called sublimation. For example, camphor, solid CO_2 (dry ice), iodine, NH_4Cl, naphthalene, etc. The white trail coming out of jets or rockets is nothing but water vapor which gets condensed to ice and is reconverted directly into water vapor. Using this property, the process of freeze drying is implemented to process foods such as instant tea, coffee powdered milk etc. This process is also known as cryodesiccation, in which substances are cooled to low temperatures of –10°C at 1 atm pressure. The water content in the substance gets converted into ice. Then the mixture is subjected to sublimation by which the water escapes in form of water vapor leaving behind the dehydrated substance.

3.18 | INTERMOLECULAR FORCES IN LIQUIDS

Many properties of liquids, such as boiling, evaporation, surface tension and viscosity, indicate the presence of intermolecular forces between molecules of liquids. For example, when water is heated, bubbles of vapor are formed by molecules that have acquired sufficient energy to overcome the intermolecular forces and enter the vapor phase. Three types of intermolecular forces are known to exist in neutral molecules. These are: dipole-dipole forces, dispersion (or London) forces and hydrogen bonding. The first two are collectively called van der Waals' forces and the third is observed in substances in which hydrogen atoms are bonded to highly electronegative species. These forces are weak in nature with strength of about 10–15% that of regular ionic or covalent bonds. These forces are briefly described here and discussed in detail in Chapter 6 (Chemical Bonding).

1. **Dipole–Dipole forces:** These are attractive intermolecular forces observed between polar molecules that results from the tendency of these molecules to align themselves such that positive end of one molecule is near the negative end of the other. For example, hydrogen chloride molecule is polar due to difference in electronegativity of hydrogen and chlorine atom. These molecules arrange themselves in a network of alignment of positive and negative ends. At room temperature, hydrogen chloride is a gas but as the temperature is lowered to –85°C, the molecules slow down and exist as liquid held together by the dipole-dipole intermolecular forces Fig. 3.36.

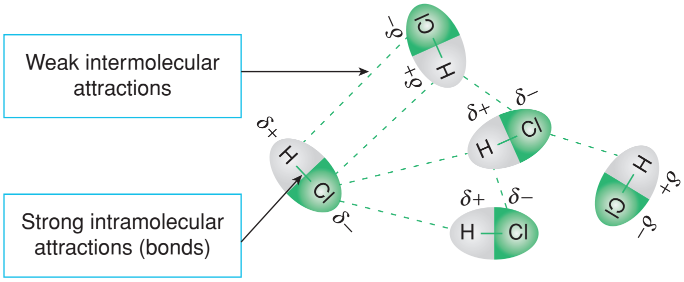

Weak intermolecular attractions
Strong intramolecular attractions (bonds)
δ+
δ–
H
Cl

Figure 3.36 Dipole–Dipole forces.

2. **Dispersion (London) forces:** These are observed in non-polar molecules where no dipole-dipole forces are present. These are weak attractive forces between molecules that arise due to instantaneous dipoles that are formed between molecules due to variation in the position of electrons during their motion around the nucleus. These intermolecular forces increase with increase in molecular weight of the molecules because these molecules are more polarizable. The electron cloud is away from the nucleus due to larger size of atoms/molecules and is hence easily distorted.
3. **Hydrogen bonding:** This is a weak to moderate attractive force that is observed in molecules where hydrogen atom is bonded to electronegative atoms such as halogens, oxygen, nitrogen, sulphur etc. Based on dispersion forces we would expect the intermolecular forces and hence the boiling point to increase in the order

$$H_2O < H_2S < H_2Se < H_2Te$$

This regular increase is observed for H_2S, H_2Se and H_2Te but water has a much higher boiling point than expected only on the basis of dispersion forces. The increased strength of intermolecular forces is due to hydrogen bonding. The hydrogen atom of one water molecule is attracted to the electron pair present on the oxygen atom of the other water molecule and a large number of molecules are linked in this manner (Fig. 3.37).

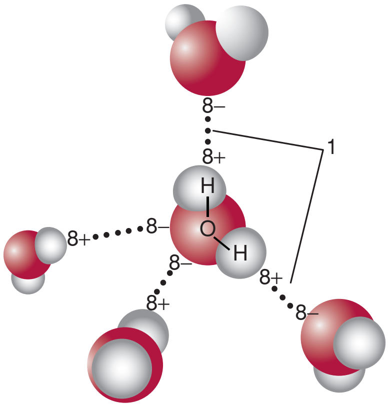


Figure 3.37 Hydrogen bonding in water.

3.19 | CHARACTERISTIC PROPERTIES OF LIQUIDS: SURFACE TENSION AND VISCOSITY

Surface Tension

A property that is especially evident for liquids is *surface tension*, which is related to the tendency of a liquid to seek a shape that yields the minimum surface area. For a given volume, the shape with the minimum surface area is a sphere – it is a principle of solid geometry. **Surface tension** *is the force that causes the surface of a liquid to contract*. It is represented by γ and is expressed as Nm^{-1}. To understand surface tension, we need to examine why molecules would prefer to be within a liquid rather than at its surface. In Fig. 3.38, we see that a molecule *within* the liquid is surrounded by densely packed molecules on all sides; whereas one at the *surface* has neighbors beside and below it, but none above. As a result, a surface molecule is attracted to fewer neighbors than one within the liquid. With this in mind, let us imagine how we might change an interior molecule to one at the surface. To accomplish this, we would have to pull away some of the surrounding molecules. Because there are intermolecular attractions, removing neighbors requires work; so there is an increase in potential energy involved. This leads to the conclusion that **a molecule at the surface has a higher potential energy than a molecule in the bulk of the liquid**.

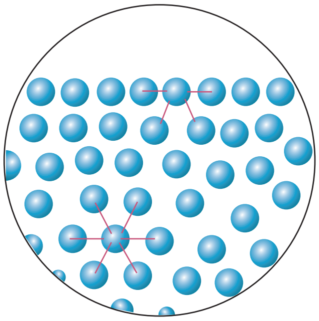


Figure 3.38 Surface tension and intermolecular attractions.

In general, a system becomes more stable when its potential energy decreases. For a liquid, reducing its surface area (and thereby reducing the number of molecules at the surface) lowers its potential energy. The lowest energy is achieved when the liquid has the smallest surface area possible (namely, a spherical shape). In more accurate terms, then, the **surface tension** of a liquid is proportional to the energy needed to expand its surface area.

The tendency of a liquid to spontaneously acquire a minimum surface area explains many common observations. Some of which are listed as follows:

1. Raindrops are like tiny spheres.
2. It causes the sharp edges of glass tubing to become rounded when the glass is softened in a flame.
3. It allows us to fill a water glass above the rim, giving the surface a rounded appearance. The surface behaves as if it has a thin, invisible "skin" that lets the water in the glass pile up, trying to assume a spherical shape. Gravity, works in opposition, tending to pull the water down. So if too much water is added to the glass, the gravitational force finally wins and the skin breaks; the water overflows.
4. Dissolved soaps reduce the surface tension of water, thus allowing the surface to expand and "wet" clothes or skin rather than form beads.
5. An insect can walk over water but would do well to avoid trying to walk on soapy water. Because of the reduced surface tension of soapy water, it would sink.

Surface tension is a property that varies with the strengths of intermolecular attractions. Liquids with strong intermolecular attractive forces have large differences in potential energy between their interior and surface molecules, and have large surface tensions. The surface tension of water is among the highest known at a given temperature. As the temperature is increased, the kinetic energy of the molecules increases and the strength of intermolecular forces decreases. Thus, the surface tension decreases with increase in temperature.

The intermolecular forces in water are hydrogen bonds which are the strongest kind of dipole–dipole attractions. The surface tension of water is roughly three times that of petrol, which consists of relatively non-polar hydrocarbon molecules able to experience only London forces.

Liquids also exhibit a phenomenon called **capillary action**, the spontaneous rising of a liquid in a narrow tube. This action results from the *cohesive forces* within the liquid and the *adhesive forces* between the liquid and the walls of the container. If the forces between the liquid and the container are greater than those within the liquid itself, the liquid will climb the walls of the container.

Note: In tall trees with height of 100 to 150 m, the water reaches the leaves at the very top; even though under atmospheric pressure, it rises in a glass tube to a maximum height of 5–6 m. This behavior can be explained on the basis of capillary action that causes water to rise from the roots of the tree to all its parts.

Viscosity

We have seen that thick syrup flows less readily or is more resistant to flow than water (both at the same temperature). Flowing is a change in the *form* of the liquid, and such resistance to a change in form is called the liquid's **viscosity**. We say that syrup is more *viscous* than water. The concept of viscosity is not confined to liquids, however, although it is with liquids that the property is most commonly associated. Solid things, even rock, also yield to forces acting to change their shapes, but normally do so only gradually and imperceptibly. Gases also have viscosity, but they respond almost instantly to form-changing forces.

When a liquid flows slowly over a fixed surface, the layer in contact with the fixed surface is stationary and the velocity of the layers increases as the distance of the layers from fixed surface increases. This type of flow in which there is a gradient of velocity in passing from one layer to the next is known as a **laminar flow**. If we consider any one layer of the liquid, the layer immediately above is moving faster than that layer and the layer immediately below is moving slower than that layer. As a result, the layer above tends to accelerate the motion while the layer below tends to retard the flow. This property by virtue of which it opposes the relative motion between different layers is known as viscosity or the "internal friction" of a material (Fig. 3.39).

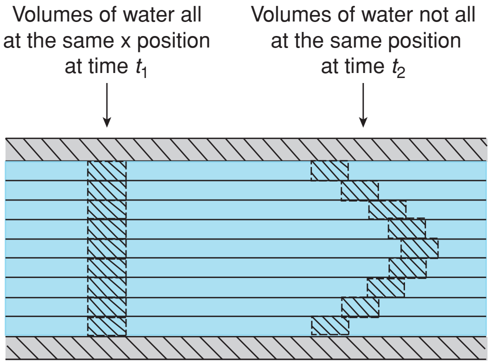

Volumes of water all at the same x position at time t_1
Volumes of water not all at the same position at time t_2

Figure 3.39 The effect of friction-like forces on laminar flow. The layers closest to the walls are slowed down most.

We have seen that, the velocity v of the flow is inversely proportional to the distance x from the fixed surface. Also, Newton showed that the viscous force is directly proportional to the surface area A of contact between the liquid and the fixed surface. Thus, the force acting on the liquid can be given by

$$F \propto \frac{Av}{x}$$

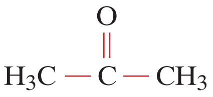
Note: We can introduce a negative sign in the relationship, simply to indicate that the direction of force opposes that of the velocity.

We can replace the term v/x by velocity gradient $\mathrm{d}v/\mathrm{d}x$ which is a measure of rate of change of velocity ($\mathrm{d}v$) with distance ($\mathrm{d}x$). Then,

$$F \propto A\frac{\mathrm{d}v}{\mathrm{d}x} \quad \text{or} \quad F = \eta A\frac{\mathrm{d}v}{\mathrm{d}x} \tag{3.62}$$

where η is a constant that depends on the nature of the liquid and is known as **coefficient of viscosity**. It is defined for a liquid as the force required per unit area to maintain a unit velocity gradient between two layers that are unit distance apart. The SI unit of viscosity coefficient is Newton second per square meter ($\mathrm{N\,s\,m^{-2}}$) or pascal second ($\mathrm{Pa\ s} = 1\mathrm{kg\ m^{-1}s^{-1}}$). In the cgs system, the unit for viscosity coefficient is poise, after the scientist Louis Poiseuille who did pioneering work on viscosity.

Viscosity is influenced both by intermolecular attractions and by molecular shape and size. For molecules of similar size, we find that as the strengths of the intermolecular attractions increase, so does the viscosity. For example, consider acetone (nail polish remover) and ethylene glycol (antifreeze), each of which contains 10 atoms.



$$H_3C-\overset{\overset{\large O}{\|}}{C}-CH_3$$

Acetone

$$HO-CH_2-CH_2-OH$$

Ethylene glycol

Ethylene glycol is more viscous than acetone, and looking at the molecular structures, it is easy to see why. Acetone contains a polar carbonyl group ($>C=O$), so it experiences dipole–dipole attractions as well as London forces. Ethylene glycol, on the other hand, contains two —OH groups. So in addition to London forces, ethylene glycol molecules also participate in hydrogen bonding (a much stronger interaction than ordinary dipole–dipole forces). Strong hydrogen bonding in ethylene glycol makes it more viscous than acetone.

Molecular size and the ability of molecules to tangle with each other is another major factor in determining viscosity. The long, entangling molecules in heavy machine oil (almost entirely a mixture of long-chain, non-polar hydrocarbons), plus the London forces in the material, give it a viscosity roughly 600 times that of water at 15°C. Vegetable oils, like the olive oil or sunflower seed oil, consist of molecules that are also large but generally non-polar. Olive oil is roughly 100 times more viscous than water.

Viscosity also depends on temperature; as the temperature drops, the viscosity increases. When water, for example, is cooled from its boiling point to room temperature, its viscosity increases by over a factor of three. As the temperature drops, molecules move more slowly and intermolecular forces become more effective at restraining flow.

Solved Example 3-54

An insect can walk over water but would do well to avoid trying to walk on soapy water.

Solution

Because of the reduced surface tension of soapy water, it would sink.

Solved Example 3-55

Why does water has higher viscosity than methyl alcohol?

Solution

Greater are the intermolecular forces, higher is the viscosity of the liquid. Since intermolecular forces in water are greater than those in methyl alcohol, water has higher viscosity than methyl alcohol.

Solved Example 3-56

Assuming ideal gas behavior, water vapor at 100°C and 1 atm has a molar volume of how many times that of liquid water under the same conditions? Given that $\rho_{\text{water}} =$ 0.9584 g cm^{-3} at 100°C.

Solution

The molar volume of water vapor is

$$V_{\text{m(water vapor)}} = \frac{RT}{p} = \frac{0.0821 \times 373}{1} = 30.62\ \text{L mol}^{-1}$$

Given that density of water at 373 K = 0.9584 g cm^{-3}. So, the volume of liquid water is

$$V = \frac{m}{\rho} = \frac{18}{0.9584} = 18.78\ \text{L mol}^{-1}$$

Therefore, the molar volume of water vapor is (30.62/18.78) = 1.6 times that of liquid water.

SOLVED OBJECTIVE QUESTIONS FROM PREVIOUS YEAR PAPERS

1. Negative deviation from ideal behavior is due to the fact that **(IIT-JEE 2003)**

(A) there exist molecular interaction and $pV/nRT > 1$
(B) there exist molecular interactions and $pV/nRT < 1$
(C) atoms have finite size and $pV/nRT > 1$
(D) atoms have finite size and $pV/nRT < 1$

Solution

(B) For positive deviation, $pV = nRT + npb$. Thus, the factor nPb is responsible for increasing the pV value above ideal value. The quantity b is actually the effective volume of molecule. So, it is the finite size of molecules that leads to the origin of b and hence positive deviation at high pressure.

2. For a monoatomic gas kinetic energy = E. The relation with rms velocity is

(A) $u_{\text{rms}} = \left(\frac{2E}{m}\right)^{1/2}$ (B) $u_{\text{rms}} = \left(\frac{3E}{2m}\right)^{1/2}$

(C) $u_{\text{rms}} = \left(\frac{E}{2m}\right)^{1/2}$ (D) $u_{\text{rms}} = \left(\frac{E}{3m}\right)^{1/2}$

(IIT-JEE 2004)

Solution

(A) Since $p = \frac{1}{3} \times \frac{m}{V} \times u_{\text{rms}}^2$, we have

$$u_{\text{rms}} = \left(\frac{3pV}{m}\right)^{1/2} \qquad (1)$$

where u_{rms} is the rms velocity for 1 molecule. Substituting $pV = kT$ in Eq. (1), we get

$$u_{\text{rms}} = \left(\frac{3kT}{m}\right)^{1/2} \qquad (2)$$

Therefore, the kinetic energy = 3/2 kT or $2E = 3kT$. Substituting in Eq. (2), we get

$$u_{\text{rms}} = \left(\frac{2\text{E}}{m}\right)^{1/2}$$

3. If methane and helium are allowed to diffuse out of a container under identical conditions of temperature and pressure, the ratio of rate of diffusion of methane to helium is

(A) 4.0 (B) 2.0
(C) 1.0 (D) 0.5 **(IIT-JEE 2005)**

Solution

(D) The ratio is

$$\frac{\text{Rate of diffusion of methane}}{\text{Rate of diffusion of helium}} = \left(\frac{4}{16}\right)^{1/2} = \frac{1}{2} = 0.5$$

4. A monatomic ideal gas undergoes a process in which the ratio of p to V at any instant is constant and equal to 1. What is the molar heat capacity of the gas?

(A) $\frac{4R}{2}$ (B) $\frac{3R}{2}$

(C) $\frac{5R}{2}$ (D) 0 **(IIT-JEE 2006)**

Solution

(A) We know that pV^{γ} = constant. Given that p/V = constant so, pV^{-1} = constant or $\gamma = -1$. Now, the molar heat capacity for any process is

$$c = C_V + \frac{R}{1-\gamma}$$

For a monoatomic gas, $C_V = (3/2)R$. Substituting, we get

$$c = \frac{3}{2}R + \frac{R}{1-(-1)} = \frac{3R+R}{2} = \frac{4R}{2} = 2R$$

5. The given graph in Fig. 3.40 represents the variation of Z (compressibility factor $= pV/nRT$) vs. p, for three real gases A, B and C. Identify the only incorrect statement.

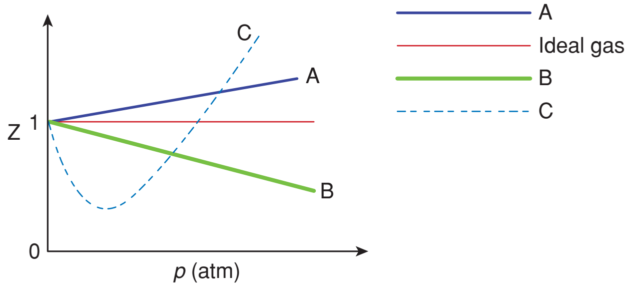


Figure 3.40

(A) For the gas A, $a = 0$ and its dependence on p is linear at all pressures.
(B) For the gas B, $b = 0$ and its dependence on p is linear at all pressures.
(C) For the gas C, which is typical real gas for which neither a nor $b = 0$. By knowing the minima and the point of intersection, with $Z = 1$, a and b can be calculated.
(D) At high pressure, the slope is positive for all real gases. **(IIT-JEE 2006)**

Solution

(B) b relates to the incompressible volume of the molecules and measures the effective size of gas molecules. $Z = pV/RT = 1$ for an ideal gas.

6. Match gases under specified conditions listed in Column 1 with their properties/laws in Column II.

Column I	Column II
(A) Hydrogen gas ($p = 200$ atm, $T = 273$ K)	(p) Compression factor $\neq 1$
(B) Hydrogen gas ($p \sim 0$, $T = 273$ K)	(q) Attractive forces are dominant
(C) CO_2 ($p = 1$ atm, $T = 273$ K)	(r) $pV = nRT$
(D) Real gas with very large molar volume	(s) $p(V - nb) = nRT$

(IIT-JEE 2007)

Solution

A → (p, s); B → (r); C → (p, q); D → (p, s)

(A) $Z = 1$ for ideal gas. At low temperature and high pressure, real gases show ideal behavior which means the equation $[p + an^2/V^2]\,[V - nb] = nRT$ reduces to $p(V - nb) = nRT$.
(B) For H_2 gas, the value of $Z = 1$ at $p = 0$ and it increases continuously on increasing p (Fig. 3.41).

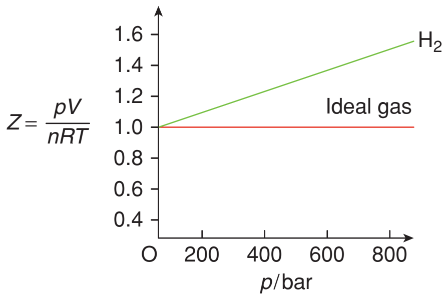


Figure 3.41

(C) CO_2 molecules have larger attractive forces, under normal conditions.
(D) As $Z = pV_m/RT$, at very large molar volume Z is not equal to 1.

7. A gas described by van der Waals equation
(A) behaves similar to an ideal gas in the limit of large molar volumes.
(B) behaves similar to an ideal gas in the limit of large pressures.
(C) is characterized by van der Waals coefficients that are dependent on the identity of the gas but are independent of the temperature.
(D) has the pressure that is lower than the pressure exerted by the same gas behaving ideally. **(IIT-JEE 2008)**

Solution

(A, C, D) The van der Waals equation is

$$\left(p + \frac{n^2 a}{V^2}\right)(V - nb) = RT$$

At low pressure, when the sample occupies a large volume, then the intermolecular forces do not play any significant role and the gas behaves virtually perfectly ideal.
Constants a and b are called van der Waals constants and their value depends on the characteristic of a gas. Value of a is a measure of magnitude of intermolecular attractive forces within the gas and is independent of temperature and pressure.

The observed p correction term is added as

$$p_{\text{ideal}} = p_{\text{real}} + \frac{an^2}{V^2}$$

Pressure exerted by real gas is lower than the pressure exerted by the ideal gas.

8. The term that corrects for the attractive forces present in a real gas in the van der Waals equation is __________

(A) nb (B) $\frac{an^2}{V^2}$

(C) $-\frac{an^2}{V^2}$ (D) $-nb$ **(IIT-JEE 2009)**

Solution

(B) The measure of forces of attraction for n moles of real gas (n^2a/V^2)

$$\left(p+\frac{n^2a}{V^2}\right)(V-nb)=nRT$$

9. At 400 K, the root mean square (rms) speed of a gas X (molecular weight = 40) is equal to the most probable speed of gas Y at 60 K. The molecular weight of the gas Y is __________ **(IIT-JEE 2009)**

Solution

(4) Given that u_{rms} (X gas) at 400 K = u_{mp} (Y gas) at 60 K, molecular weight $M_1 = 40$, $M_2 = ?$, $T_1 = 400$ K and $T_2 = 60$ K. Therefore,

$$\sqrt{\frac{3RT_1}{M_1}}=\sqrt{\frac{2RT_2}{M_2}}$$

$$\sqrt{\frac{400\times3\times R}{40}}=\sqrt{\frac{2\times R\times60}{M_2}}$$

Solving, we get $M_2 = 4$.

10. To an evacuated vessel with movable piston under external pressure of 1 atm., 0.1 mol of He and 1.0 mol of an unknown compound (vapor pressure 0.68 atm at 0°C) are introduced. Considering the ideal gas behavior, the total volume (in liters) of the gases at 0°C is close to __________. **(IIT-JEE 2011)**

Solution

(7) Let V be the volume of the gas. Applying ideal gas equation $pV = nRT$, we get

$$n=\frac{pV}{RT}=0.68\times\frac{V}{RT}$$

So, the total moles of gas present in the vessel will be = $(0.1 + 0.68 \times V/RT)$

Again applying ideal gas equation $pV = nRT$, we get

$$1\times V=\left(0.1+0.68\times\frac{V}{RT}\right)RT=0.1RT+0.68V$$

Solving, we get

$$V=0.1\times0.082\times\frac{273}{0.32}=7$$

11. According to kinetic theory of gases,

(A) collisions are always elastic.
(B) heavier molecules transfer more momentum of the wall of the container.
(C) only a small number of molecules have very high velocity.
(D) between collisions, the molecules move in straight lines with constant velocities. **(IIT-JEE 2011)**

Solution

(A, B, C, D)

(A) Collisions of gas molecules are perfectly elastic which means that the total energy of the molecules before and after the collision remains the same.
(B) Heavier particles transfer more momentum because momentum depends on the mass.
(C) Only a small number of molecules possess very high velocity.
(D) Particles of gas move in all possible directions in straight lines. The distribution of speed remains constant at a particular temperature.

12. For one mole of a van der Waals gas when $b = 0$ and $T = 300$ K, the pV vs. $1/V$ plot is shown in Fig. 3.42. The value of the van der Waals constant a (atm L^2 mol^{-2}) is

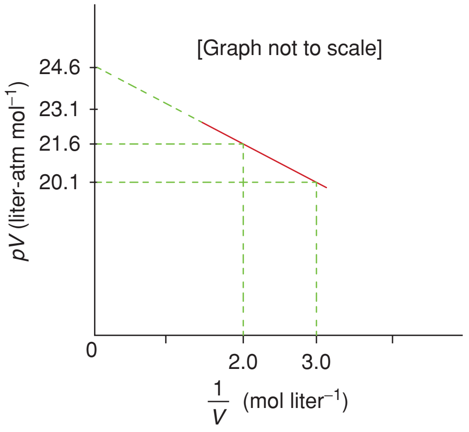


Figure 3.42

(A) 1.0 (B) 4.5
(C) 1.5 (D) 3.0 **(IIT-JEE 2012)**

Solution

(C) van der Waals equation is

$$\left(p+\frac{a}{V^2}\right)(V-b)=RT$$

but it is given that $b = 0$. So, the equation reduces to

$$\left(p+\frac{a}{V^2}\right)V=RT\Rightarrow pV=-\frac{a}{V}+RT$$

Comparing it with a straight line equation we get slope as $-a$. Calculating the slope, we get

$$\frac{24.6-20.1}{3.0-0}=1.5\Rightarrow a=1.5$$

Passage for Questions 13 and 14: **X** and **Y** are two volatile liquids with molar weights of 10 g mol^{-1} and 40 g mol^{-1}, respectively. Two cotton plugs, one soaked in **X** and the other soaked in **Y**, are simultaneously placed at the ends of a tube of length L = 24 cm, as shown in Fig. 3.43. The tube is filled with an inert gas at 1 atmosphere pressure and a temperature of 300 K. Vapors of **X** and **Y** react to form a product which is first observed at a distance d cm from the plug soaked in X. Take **X** and **Y** to have equal molecular diameters and assume ideal behaviour for the inert gas and the two vapors.

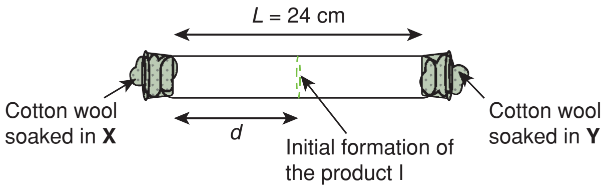

L = 24 cm
Cotton wool soaked in **X**
d
Initial formation of the product I
Cotton wool soaked in **Y**

Figure 3.43

13. The value of d in cm (shown in Fig. 3.43), as estimated from Graham's law, is
(A) 8 (B) 12 (C) 16 (D) 20
(JEE Advanced 2014)

Solution

(C) Using Graham's law of diffusion we have that for identical conditions, rate of diffusion varies inversely with square root of mass of the gases. So,

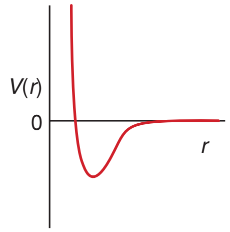
$$\frac{x}{24-x}=\left(\frac{40}{10}\right)^{1/2} \Rightarrow x=16$$

14. The experimental value of d is found to be smaller than the estimate obtained using Graham's law. This is due to
(A) larger mean free path for **X** as compared to that of **Y**
(B) larger mean free path for **Y** as compared to that of **X**
(C) increased collision frequency of **Y** with the inert gas as compared to that of **X** with the inert gas
(D) increased collision frequency of **X** with the inert gas as compared to that of **Y** with the inert gas
(JEE Advanced 2014)

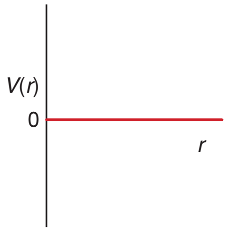
Solution

(D) Collision frequency of **X** is greater than **Y**.

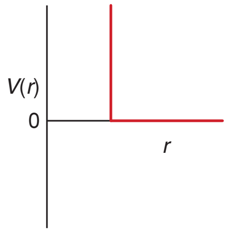
15. One mole of a monoatomic real gas satisfies the equation $p(V-b) = RT$ where b is a constant. The relationship of interatomic potential $V(r)$ and interatomic distance r for the gas is given by



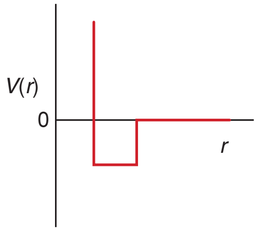
(A)



(B)



(C)



(D)

(JEE Advanced 2015)

Solution

(C) As interatomic forces are absent; the interatomic potential does not vary with interatomic distance.

16. According to the kinetic theory of gases, in an ideal gas, between two successive collisions a gas molecule travels
(A) in a circular path.
(B) in a wavy path.
(C) in a straight line path.
(D) with an accelerated velocity. **(AIEEE 2003)**

Solution

(C) This is one of the assumption of kinetic theory of gases.

17. As the temperature is raised from 20°C to 40°C, the average kinetic energy of neon atoms changes by a factor of which of the following?
(A) 1/2 (B) 2
(C) 313/293 (D) $\sqrt{313/293}$
(AIEEE 2004)

Solution

(C) $T_1 = 273+20 = 293$ K and $T_2 = 273+40 = 313$ K. As the kinetic energy is proportional to the temperature, we have

$$\frac{E_1}{E_2}=\frac{T_1}{T_2}=\frac{293}{313} \Rightarrow \frac{E_2}{E_1}=\frac{313}{293}$$

18. In van der Waals equation of state of the gas law, the constant b is a measure of
(A) intermolecular repulsions.
(B) intermolecular collisions per unit volume.
(C) volume occupied by the molecules.
(D) intermolecular attractions. **(AIEEE 2004)**

Solution

(C) Volume occupied by the molecules
The van der Waals equation for 1 mol of gas is:

$$\left(p+\frac{a}{V^2}\right)(V-b)=RT$$

where b is the measure of effective size of the gas molecules. It is also called co-volume or excluded volume.

19. Which one of the following statements is NOT true about the effect of an increase in temperature on the distribution of molecular speeds in a gas?
(A) The most probable speed increases.
(B) The fraction of the molecules with the most probable speed increases.
(C) The distribution becomes broader.
(D) The area under the distribution curve remains the same as under the lower temperature. **(AIEEE 2005)**

Solution

(B) According to Maxwell's distribution, the most probable velocity increases as the fraction of molecules possessing most probable velocity decreases.

20. An ideal gas is allowed to expand both reversibly and irreversibly in an isolated system. If T_i is the initial temperature and T_f is the final temperature, which of the following statements is correct? **(AIEEE 2006)**

(A) $(T_f)_{irrev} > (T_f)_{rev}$
(B) $T_f > T_i$ for reversible process but $T_f = T_i$ for irreversible process.
(C) $(T_f)_{rev} = (T_f)_{irrev}$
(D) $T_f = T_i$ for both reversible and irreversible processes.

Solution

(D) In an ideal gas, there are no intermolecular forces of attraction. So, $T_f = T_i$ for both reversible and irreversible processes.

21. Equal masses of methane and oxygen are mixed in an empty container at 25°C. The fraction of the total pressure exerted by oxygen is ________.

(A) $\frac{1}{2}$ (B) $\frac{2}{3}$
(C) $\frac{1}{3} \times \frac{273}{298}$ (D) $\frac{1}{3}$ **(AIEEE 2007)**

Solution

(D) Let the mass of methane and oxygen be x because they are equimolar (same masses) grams

$$\text{Mole fraction of oxygen} = \frac{\text{Number of moles of oxygen}}{\text{Total number of moles}}$$

where number of moles of oxygen = $x/32$ (molecular mass of O_2 is 32)
Number of moles of methane = $x/14$ (molecular mass of CH_4 is 16)
Therefore, mole fraction of oxygen is

$$\frac{x/32}{(x/32)+(x/16)} = \frac{1}{3}$$

Let the total pressure be p. Then, partial pressure of oxygen is

$$p_{O_2} = \text{Mole fraction of oxygen} \times p_{\text{total}} = \frac{1}{3} \times p = \frac{p}{3}$$

22. Two liquids X and Y form an ideal solution. At 300 K, vapor pressure of the solution containing 1 mol of X and 3 mol of Y is 550 mm Hg. At the same temperature, if 1 mol of Y is further added to this solution, vapor pressure of the solution increases by 10 mm Hg. Vapor pressure (in mm Hg) of X and Y in their pure states will be, respectively,

(A) 400 and 600 (B) 500 and 600
(C) 200 and 300 (D) 300 and 400

(AIEEE 2009)

Solution

(A) Mole fraction of X and Y are

$$\text{Mole fraction of X} = \frac{1}{1+3} = \frac{1}{4}$$

$$\text{Molefraction of Y} = \frac{3}{1+3} = \frac{3}{4}$$

Total pressure = Partial pressure of X × Mole fraction of X + Partial pressure of Y × Mole fraction of Y

$$550 = \frac{p^\circ_X}{4} + \frac{3p^\circ_Y}{4} \qquad (1)$$

$$550 \times 4 = p^\circ_X + 3p^\circ_Y$$

When one mole of Y is added then mole fraction of X becomes $1/(1+4) = 1/5$ and mole fraction of Y becomes $4/(1+4) = 4/5$. Now, the total pressure given as

$$560 = \frac{p^\circ_X}{5} + \frac{4p^\circ_Y}{5} \qquad (2)$$

$$560 \times 5 = p^\circ_X + 4p^\circ_Y$$

Solving Eqs. (1) and (2), we get $p^\circ_X = 400$ mm Hg and $p^\circ_Y = 600$ mm Hg.

23. If 10^{-4} dm^3 of water is introduced into a flask at 300 K, how many moles of water are in the vapor phase when equilibrium is established? (Given: Vapor pressure of H_2O at 300 K is 3170 Pa; R = J K^{-1}mol^{-1})

(A) 1.27×10^{-3} mol (B) 5.56×10^{-3} mol
(C) 1.53×10^{-2} mol (D) 4.46×10^{-2} mol

(AIEEE 2010)

Solution

(A) Using ideal gas equation $pV = nRT$, we get

$$n = \frac{pV}{RT} = \frac{3170 \times 10^{-5}\ \text{atm} \times 1\ \text{L}}{0.0821\ \text{L atm K}^{-1}\ \text{mol}^{-1} \times 300\ \text{K}}$$
$$= 1.27 \times 10^{-3}\ \text{mol}$$

24. A vessel at 100 K contains CO_2 with a pressure of 0.5 atm. Some of the CO_2 is converted into CO on the addition of graphite. If the total pressure at equilibrium is 0.8 atm, the value of K_p is ________.

(A) 3 atm (B) 0.3 atm
(C) 0.18 atm (D) 1.8 atm **(AIEEE 2011)**

Solution

(D) The reaction is $CO_2(g) + C(s) \rightleftharpoons 2CO(g)$

Initial concentration	p	0
At equilibrium	$p - X$	$2X$

Also, $p \propto n$. Now,

$$\frac{p}{p+X} = \frac{0.5}{0.8}$$

Solving, we get $X = 0.3$. Now, $p_{CO_2} = p - X = 0.5 - 0.3 = 0.2$ atm and $p_{CO} = 2X = 2 \times 0.3 = 0.6$. The value of K_p can be calculated as

$$K_p = \frac{p^2_{CO}}{p_{CO_2}} = \frac{0.6 \times 0.6}{0.2} = 1.8\ \text{atm}$$

25. Chlorine is more easily liquefied than ethane because ("*a*" and "*b*" are van der Waals constants for gases).

(A) a and b for $Cl_2 <$ a and b for C_2H_6
(B) a for $Cl_2 <$ a for C_2H_6 but b for $Cl_2 >$ a for C_2H_6
(C) a for $Cl_2 >$ a for C_2H_6 but b for $Cl_2 <$ a for C_2H_6
(D) a and b for $Cl_2 >$ a and b for C_2H_6

(AIEEE 2011)

Solution

(C) Ease of liquefaction ∝ a/b

For easily liquefiable gas, more should be the value of a and less should be the value of b.

For ethane, $a = 5.49$, $b = 0.0638$ and for Cl_2, $a = 6.49$, $b = 0.0562$.

26. The compressibility factor for a real gas at high pressure is

(A) $1 + RT/pb$
(B) 1
(C) $1 + pb/RT$
(D) $1 - pb/RT$

(AIEEE 2012)

Solution

(C) According to van der Waals equation, we have

$$\left(p+\frac{a}{V^2}\right)(V-nb)=RT$$

At high pressure, a/V^2 is very large so it is neglected in comparison to p. Now, $p(V - b) = RT$ for 1 mol of a gas, that is, $n = 1$. Also,

$$pV = RT + pb$$

or

$$\frac{pV}{RT}=1+\frac{pb}{RT}$$

where $Z = 1 + pb/RT$ is known as the compressibility factor.

27. For gaseous state, if most probable speed is denoted by C^*, average speed by C and mean square speed by C then for a large number of molecules the ratio of these speeds are

(A) $C^*:\bar{C}:C = 1.128:1.225:1$
(B) $C^*:\bar{C}:C = 1:1.128:1.225$
(C) $C^*:\bar{C}:C = 1:1.125:1.128$
(D) $C^*:\bar{C}:C = 1.225:1.128:1$

(JEE Main 2013)

Solution

(B) We know that $C^*=\sqrt{\frac{2RT}{M}}, \bar{C}=\sqrt{\frac{8RT}{\pi M}}, C=\sqrt{\frac{3RT}{M}}$

Thus, we have $C^*:\bar{C}:C=\sqrt{2}:\sqrt{\frac{8}{\pi}}:\sqrt{3}$

Solving, we get $C^*:\bar{C}:C = 1.414:1.595:1.732 = 1:1.128:1.225$

28. If Z is a compressibility factor, van der Waals equation at low pressure can be written as

(A) $Z=1+\frac{RT}{pb}$
(B) $Z=1-\frac{a}{VRT}$
(C) $Z=1-\frac{Pb}{RT}$
(D) $Z=1+\frac{Pb}{RT}$

(JEE Main 2014)

Solution

(B) We know that compressibility factor is given by $Z=\frac{pV}{RT}$

For one mole of gas, we have

$$\left(p+\frac{a}{V^2}\right)(V-b)=RT$$

At low pressure, volume is very high, so $V \gg b$ and thus $V - b \approx b$.

$$\left(p+\frac{a}{V^2}\right)(V)=RT \Rightarrow pV=RT-\frac{a}{V}$$

$$\Rightarrow \frac{pV}{RT}=1-\frac{a}{VRT} \Rightarrow Z=1-\frac{a}{VRT}$$

REVIEW QUESTIONS

1. A gas occupies a volume of 3.86 L at 0.750 atm. At what pressure will the volume be 4.86 L?

2. What is the volume of the gas in a balloon at –195°C if the balloon has been filled to a volume of 5.0 L at 25°C?

3. A highly viscous liquid was heated from 10°C to 14°C. What will be the percent decrease in viscosity.

4. Decide which law predicts the behavior of gas in each of the following conditions:

(a) A balloon in the winter being moved from indoors to outdoors.
(b) A car tyre pressure fluctuating over the course of a year.
(c) Dry ice being used in a fog machine to cover a stage with mist.
(d) Piston movement in an internal combustion engine.

5. Which of the following substances can be liquefied just by compression at room temperature? Give the condition necessary for liquefaction for the other gases.

Substance	Critical Temperature (K)	Critical Pressure (atm)
Nitrogen	126	33.5
Ethanol	516	63
Butane	272.5	38
Sulphur dioxide	431	78

6. Between H_2 and O_2, which will move with a higher speed? Calculate the temperature at which the speed of oxygen equals that of hydrogen at 40 K.

7. NaCl is soluble is soluble in H_2O but is not insoluble in CCl_4. Explain on the basis of ion–dipole interactions.

8. Give two practical applications indicating the useful property of incompressiblity in liquids.

9. Differentiate between a barometer and a manometer?

10. What volume of "wet" methane would you have to collect at 20.0°C and 742 mm Hg to be sure that the sample contains 244 mL of dry methane (also at 742 mm Hg)?

11. Using Boyle's law and Charles' law, derive combined gas law.

12. Why do N_2O and CO_2 have the same rate of diffusion under same conditions of temperature and pressure?

13. What would happen to a balloon if the collisions between gas molecules were not perfectly elastic? What would happen to a balloon if the gas molecules were in a state of constant motion but the motion was not random?

14. Compare the rates of diffusion of $^{235}UF_6$ and $^{238}UF_6$.

15. CO_2 is heavier than O_2 and N_2 gases present in the air, but it does not form the lower layer of the atmosphere. Why?

16. The molecular speeds of gaseous molecules are analogous to those of rifle bullets. Then why is the odor of a gas not detected so fast?

17. What is the ratio of average kinetic energy of oxygen molecules to that of ozone molecules at 27°C?

18. Differentiate between total kinetic energy and translational kinetic energy? For what type of molecules, the two are equal?

19. Out of N_2 and NH_3, which one will have greater value for van der Waals constant "*a*" and which one will have greater value for van der Waals constant "*b*"?

20. The critical temperature (T_C) and critical pressure (p_C) of CO_2 are 30.98°C and 73 atm, respectively. Can CO_2 (g) be liquefied at 32°C and 80 atm pressure?

21. Why are falling liquid drops spherical?

22. What happens if a liquid is heated to the critical temperature of its vapors?

23. Prove that the excluded volume "*b*" is four times the actual volume of the gas molecules.

NUMERICAL PROBLEMS

1. How many number of moles and molecules of O_2 are there in 64 g O_2? What is the mass of one molecule of O_2?

2. Two moles of ammonia occupied a volume of 5 L at 27°C then calculate the pressure of the gas if it obeys van der Waals equation given a = 4.17 atm L^2 mol^{-1} and b = 0.037 L mol^{-1}.

3. A gaseous system has a volume of 580 cm^3 at a certain pressure. If its pressure is increased by 0.96 atm, its volume becomes 100 cm^3. Determine the pressure of the system.

4. A balloon filled with helium raises to a certain height at which it gets fully inflated to a volume of 1×10^5 L. If at this altitude temperature and atmospheric pressure is 268 K and 2×10^{-3} atm, respectively, what weight of helium is required to fully inflate the balloon?

5. Time taken to diffuse 40 mL of oxygen gas is 20 s. Calculate the time required to diffuse 120 mL of CH_4?

6. Compressibility factor (Z) for N_2 at −50°C and 800 atm pressure is 1.95. Calculate the number of moles of N_2 gas required to fill a gas cylinder of 100 mL capacity under the given conditions.

7. A balloon blown up has a volume of 500 mL at 5°C. The volume is decreases to seven-eighth of its maximum stretching capacity.
- **(a)** Will it burst at 30°C
- **(b)** Calculate the minimum temperature above which it will burst.

8. 1.0 L of a mixture of CO and CO_2 is taken. The mixture is passed through the tube containing red hot charcoal. The volume now becomes 1.6 L measured under the same conditions. Find the composition of the mixture by volume.

9. A sample of cool gas contains 50% hydrogen, 30% marsh gas (CH_4), 14% carbon monoxide and 6% ethylene. 100 mL of this coal is mixed with 150 mL of oxygen and mixture is exploded. What will be the volume and composition of the resulting gas when cooled to the original temperature?

10. Two moles ammonia gas are enclosed in a vessel of 5 L capacity at 27°C. Calculate the pressure exerted by the gas assuming that:
- **(a)** the gas behaves as an ideal gas.
- **(b)** the gas behaves as a real gas (a = 4.17 L^2 atm mol^{-1}, b = 0.37 L mol^{-1})

11. The density of the vapor of a substance at 1 atm pressure and 500 K is 0.36 kg m^{-3}. The vapor effuses through a small hole at a rate of 1.33 times faster than oxygen under the same conditions.
- **(a)** Determine (i) molar weight; (ii) molar volume; (iii) compression factor (Z) of the vapor and (iv) which forces among the gas molecules are dominating, the attractive or the repulsive.
- **(b)** If the vapor behalves ideally at 1000 K, determine the average translational K.E. of a molecule.

12. Calculate the compressibility factor for CO_2 if one mole of it occupies 0.4 L at 300 K and 40 atm. Comment on the result.

13. Two gases A and B having molecular weights 60 and 45, respectively, are enclosed in a vessel. The weight of A is 0.50 g and that of B is 0.2 g. The total pressure of the mixture is 750 mm Hg. Calculate the partial pressure of the two gases.

14. A container has SO_2 gas at 2 atm pressure in a vessel of V L capacity, if the number of moles of SO_2 are doubled in the same container at same temperature and volume. Calculate new pressure in the container.

15. A tank is filled with gas to a pressure of 5 atm at 10°C. The safety valve on the tank is set for 10 atm pressure. To what temperature must the tank be heated in order to below the safety valve?

16. The compressibility factor for CO_2 gas at 273 K and 100 atm pressure is 0.2005. Calculate the volume occupied by 0.2 mol of CO_2 at 100 atm and 273 assuming **(a)** ideal gas nature and **(b)** real gas nature.

17. The density of the mixture of nitrogen and oxygen is 1.15 g L^{-1} at 750 mm Hg at 27°C. Calculate the percentage composition of these gases in the mixture. Assume the gases behave ideally.

18. 100 mL of mixture of methane and acetylene was exploded with excess of oxygen. After explosion and cooling the mixture was treated with KOH, when the reduction 135 mL was observed. Find the volumetric composition of the mixture. All the volumes are measured at the same temperature and pressure.

19. Calculate the volume occupied by 4.0245×10^{23} molecules of O_2 at 27°C having pressure of 700 torr.

20. Calculate the moles, molecules and weight of hydrogen gas contained in a 10 L flask at a pressure of 75 cm Hg and at temperature 25°C.

21. The compressibility factor for a given real gas is 0.927 at 273 K and 100 atm. Calculate the amount of O_2 required to fill a gas cylinder of 100 L capacity under given conditions (molecular weight of gas = 30)

22. The density of oxygen at STP is 0.00143 g mL^{-1}. Find the rms velocity, average velocity and most probable velocity.

23. Calculate the volume correction and pressure correction for 4.4 g CO_2 kept in 1 L flask. Given $a = 3.6$ atm L^2 mol^{-2} and $b = 0.04$ L mol^{-1} for CO_2.

24. Two bulbs A and B of equal capacity are filled with He and SO_2, respectively, at the same temperature.
   - **(a)** If the pressure in two bulb is same, what will be the ratio of the velocities of the molecules of two gases?
   - **(b)** At what temperature will the velocity of SO_2 molecules becomes half of the velocity of the He molecules at 27°C?
   - **(c)** How will the velocities be affected if the volume of B becomes 4 times that of A?
   - **(d)** How will the velocities be affected if half of the molecules of SO_2 are removed from B?

25. Total pressure exerted by a mixture of two gases in a container is 500 mm Hg. The pressure of 1st gas is 200 mm Hg. Then calculate mole fraction of each gas and partial pressure of gas.

26. Calculate the temperature of gas if it obeys van der Waals equation from the following data. A flask of 25 L contains 10 mol of a gas under 50 atm. Given $a = 5.46$ atm L^2 mol^{-2} and $b = 0.031$ L mol^{-1}

27. 10 mL of gaseous hydrocarbon are exploded with 100 mL of oxygen. The residual gas, on cooling, is found to measure 95 mL of which 20 mL are absorbed by KOH solution and remained by pyrogallol solution. Determine the molecular formula of hydrocarbon.

28. A gas which is contained in a closed container volume of 20 L at 300 K. If temperature is increased by 50% then calculate % change in volume assuming pressure constant.

29. Pressure as low as 10^{-9} torr (1 torr = 1/760 atm) are obtained in high vacuum systems at 30°C. How many gaseous molecules per mL are present in such a vacuum?

30. Temperature at the foot of a mountain is 30°C and pressure is 760 mm Hg whereas at the top of the mountain these are 0°C and 710 mm Hg. Compare the densities of the air at the foot and at the top of the mountain.

31. The volume of 0.0227 mol of gas is 550 mL at a pressure of 1.25 atm and a temperature of 22°C.
   - **(a)** What is the volume at 1.25 atm and 44°C?
   - **(b)** What is the volume if 0.0115 mol of gas is added at the same T and p?
   - **(c)** What is the pressure at 122°C if the volume remains 550 mL?
   - **(d)** What is the pressure at 22°C if the volume expands to 825 mL?
   - **(e)** What is the volume when you convert to STP conditions?

32. Calculate the average volume available to a molecule in a sample of nitrogen gas at STP. What is the average distance between neighboring molecules if a nitrogen molecule is assumed to be spherical?

ADDITIONAL OBJECTIVE QUESTIONS

Single Correct Choice Type

1. The compressibility of a gas is less than unity at STP. Therefore,

(A) $V_m > 22.4$ L
(B) $V_m < 22.4$ L
(C) $V_m = 22.4$ L
(D) $V_m > 44.8$ L

2. A gaseous compound X contained 44.4% C, 51. 9% N and 3.7% H. Under the same conditions, 30 cm^3 of X diffused through a pinhole in 25 s and the same volume of H_2 diffused in 4.81 s. The molecular formula of X is

(A) C_2H_2N
(B) $C_2H_4N_2$
(C) $C_2H_2N_2$
(D) $C_4H_2N_2$

3. Four particles have velocities 1, 0, 2, 3 ms^{-1}. The root mean square of the particles is (in m s^{-1})

(A) 3.5
(B) $\sqrt{3.5}$
(C) 1.5
(D) $\sqrt{14/3}$

4. A mixture of methane and ethene in the molar ratio of x:y has a mean molar mass of 20. What would be the mean molar mass if the gases are mixed in the molar ratio of y:x?

(A) 22 g mol^{-1}
(B) 24 g mol^{-1}
(C) 20.8 g mol^{-1}
(D) 19 g mol^{-1}

5. A flask of capacity one L contains NH_3 at 1 atm and 25°C. A spark is passed through until all the NH_3 is decomposed into N_2 and H_2. Calculate the pressure of gases left at 25°C.
(A) 2 atm (B) 0.5 atm
(C) 1.5 atm (D) 1 atm

6. The rms speed of the gas molecule at temperature 27 K and pressure 1.5 bar is 1×10^4 cm s^{-1}. If both temperature and pressure are raised three times, the rms speed of the gas molecules will be
(A) 9×10^4 cm s^{-1} (B) 3×10^4 cm s^{-1}
(C) $\sqrt{3} \times 10^4$ cm s^{-1} (D) 1×10^4 cm s^{-1}

7. Since the atomic weights of C, N and O are 12, 14 and 16u, respectively, among the following pair, the pair that will diffuse at the same rate is
(A) carbon dioxide and nitrous oxide.
(B) carbon dioxide and nitrogen peroxide.
(C) carbon dioxide and carbon monoxide.
(D) nitrous oxide and nitrogen peroxide.

8. SO_3 (g) decomposes according to the equation $2SO_3(g) \rightarrow 2SO_2(g) + O_2(g)$. A sealed container contains 0.5 mol of SO_3 gas at 100°C and 2 atm pressure. What would be the pressure in the container if the SO_3 gas is decomposed completely according to the above equation and the temperature were maintained at 100°C?
(A) 0.5 atm (B) 1.0 atm
(C) 2.0 atm (D) 3.0 atm

9. If the pressure of a given mass of gas is reduced to half and temperature is doubled simultaneously, the volume will be
(A) same as before.
(B) twice as before.
(C) four times as before.
(D) one fourth as before.

10. A general form of equation of state for gases is $pV = RT\left[A + \frac{B}{V} + \frac{C}{V^2} + \ldots\right]$ where V is the molar volume of the gas and A, B, C, … are constants for the gas. The values of A and B if the gas obeys van der Waals equation are, respectively.
(A) $\frac{a}{RT}, b$ (B) $\frac{2a}{RT}, b$
(C) $1, b - \frac{a}{RT}$ (D) $1, \frac{a}{27b}$

11. I, II, III are three isotherms, respectively, at T_1, T_2 and T_3 as shown in Fig. 3.44. The temperatures will be in the order:
(A) $T_1 = T_2 = T_3$ (B) $T_1 < T_2 < T_3$
(C) $T_1 > T_2 > T_3$ (D) $T_1 > T_2 = T_3$

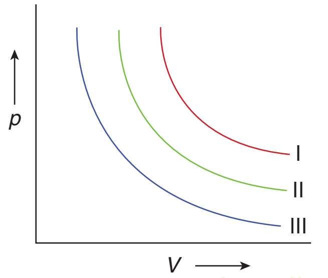


Figure 3.44

12. A certain gas diffuses from two different vessels A and B. The vessel A has a circular orifice while vessel B has a square orifice of length equal to the radius of the orifice of vessel A. Calculate the ratio of the rates of diffusion of the gas from vessel A to vessel B, assuming same temperature and pressure is
(A) π (B) $1:\pi$
(C) 1:1 (D) 2:1

13. What would happen to the volume of a balloon filled with 0.357 L of H_2 gas collected at 741.3 mm Hg if the atmospheric pressure increased to 758.1 mm Hg?
(A) 0.45 L (B) 0.35 L
(C) 0.25 L (D) 0.15 L

14. A gas bulb containing air is connected to an open limb manometer at 27°C and at 750 mm Hg. Assuming that initially the level of Hg in the both limbs were same. The bulb was heated to 77°C, what will be difference in the levels of Hg in two limbs? (Assume the volume difference of the gas produced is negligible at higher temperature).
(A) 7.5 cm Hg (B) 8 cm Hg
(C) 6 cm Hg (D) 12.5 cm Hg

15. The critical temperature and critical pressure of a gas obeying van der Waals equation are 30°C and 73 atm, respectively. Its van der Waals constant, b (in L s mol^{-1}) is, therefore,
(A) 0.500 (B) 0.060
(C) 0.265 (D) 0.128

16. The van der Waal constants for HCl are a = 371.843 kPa and b = 40.8 cm^{3}mol^{-1}. The critical temperature is
(A) 324.8 K (B) 424.8 K
(C) 350.9 K (D) 450.9 K

17. A certain volume of argon gas (molar weight = 40 g mol^{-1}) requires 45 s to effuse through a hole at a certain pressure and temperature. The same volume of another gas of unknown molecular weight requires 60 s to pass through the same hole under the same conditions of temperature and pressure. The molecular weight of the gas is
(A) 53 g mol^{-1} (B) 35 g mol^{-1}
(C) 71 g mol^{-1} (D) 120 g mol^{-1}

18. 400 cm^3 of oxygen at 27°C were cooled –3°C without change in pressure. The contraction in volume will be
(A) 40 cm^3 (B) 30 cm^3
(C) 44.4 cm^3 (D) 60 cm^3

19. Consider the following statements: The mean free path of gas molecules
(I) decreases with increase in concentration.
(II) increases with decrease in pressure at constant temperature.
(III) decrease with increase in molecular size.
(A) I, II (B) I, III
(C) II, III (D) I, II, III

20. At 47°C and 16.0 atm, the molar volume of NH_3 gas is about 10% less than the molar volume of an ideal gas. Which of the following is the true reason?
(A) NH_3 decompose to N_2 and H_2 at 47°C.
(B) The force of attraction between NH_3 molecules is significant at this temperature and pressure.

(C) The volume occupied by NH_3 molecules themselves is a significant fraction of the volume of the container at this temperature and pressure.
(D) At 16 atm, NH_3 molecules no longer move randomly.

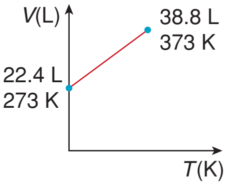
21. How much time would it take to distribute one Avogadro number of wheat grains if 10^{10} grains are distributed in each second?
(A) 4×10^2 year (B) 9×10^6 year
(C) 6×10^4 year (D) 1.9×10^6 year

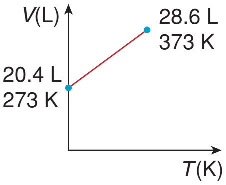
22. At what temperature will the rate of effusion of N_2 be 1.625 times the rate of effusion of SO_2 at 500°C?
(A) 273 K (B) 830 K
(C) 110 K (D) 173 K

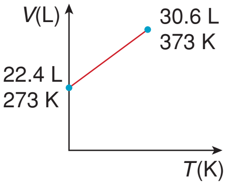
23. 2.9 g of gas at 95°C occupied the same volume as 0.184 g of dihydrogen at 17°C, at the same pressure. What is the molar mass of the gas?
(A) 120 g mol^{-1} (B) 20 g mol^{-1}
(C) 80 g mol^{-1} (D) 40 g mol^{-1}

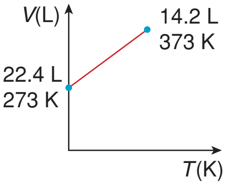
24. The compressibility of a gas is less than unity at STP. Therefore,
(A) $V_m > 22.4$ L (B) $V_m < 22.4$ L
(C) $V_m = 22.4$ L (D) $V_m = 44.8$ L

25. Which of the following V, T plots represents the behavior of one mole of an ideal gas at one atmosphere?

(A) 

(B) 

(C) 

(D) 

26. Equal weights of methane and oxygen are mixed in an empty container at 25°C. The fraction of the total pressure exerted by oxygen is
(A) $\frac{1}{3}$ (B) $\frac{1}{2}$
(C) $\frac{2}{3}$ (D) $\frac{1}{3} \times \frac{273}{298}$

27. The root mean square velocity of one mole of a monoatomic gas having molar mass M is $u_{rms.}$ The relation between the average kinetic energy (E) of the gas and u_{rms} is
(A) $u_{rms} = \frac{\sqrt{3E}}{2M}$ (B) $u_{rms} = \frac{\sqrt{2E}}{3M}$
(C) $u_{rms} = \frac{\sqrt{2E}}{M}$ (D) $u_{rms} = \frac{\sqrt{E}}{3M}$

28. 40 mL of mixture of H_2 and O_2 was placed in a gas burette at 18°C and 1 atm. A spark was produced so that the formation of water was complete. The remaining pure gas had a volume of 10 mL at 18°C and 1 atm. If the remaining gas was H_2, what was initial mole % of H_2 in mixture?
(A) 75% (B) 25%
(C) 60% (D) 45%

29. 80 mL of oxygen is added to 50 mL of a mixture of H_2, C_2H_2 and CO, after which the total mixture is burnt. The volume of the cooled mixture after combustion measures 65 mL. This is reduced to 15 mL by treatment with aqueous KOH solution. Calculate the volume of each gas in the original mixture.
(A) 20 mL of H_2, 20 mL of C_2H_2, 10 mL of CO.
(B) 10 mL of H_2, 20 mL of C_2H_2, 20 mL of CO.
(C) 15 mL of H_2, 15 mL of C_2H_2, 20mL of CO.
(D) 10 mL of H_2, 15 mL of C_2H_2, 25mL of CO.

30. The kinetic energy (in kcal) of 80 g of methane gas at 227°C is
(A) 15 (B) 2.5
(C) 25 (D) 7.5

31. If a certain mass of gas is expanded at constant temperature,
(A) the pressure of the gas decreases.
(B) the kinetic energy of the gas molecules increases.
(C) the kinetic energy of the molecules decreases.
(D) the number of molecules of the gas increases.

32. The rate of effusion of helium gas at a pressure of 1000 torr is 10 torr min^{-1}. What will be the rate of effusion of hydrogen gas at a pressure of 2000 torr at the same temperature?
(A) 20 torr min^{-1} (B) 40 torr min^{-1}
(C) $20\sqrt{2}$ torr min^{-1} (D) 10 torr min^{-1}

33. A closed vessel contains equal number of oxygen and hydrogen molecules. Consider the following statements:
(I) The average speed of hydrogen molecules is greater.
(II) The two gases have different average energies.
(III) Hydrogen molecules strike the walls more often.
(IV) Weight of hydrogen is one-eighth of the weight of oxygen.

The incorrect statements are
(A) I and II (B) II and III
(C) I and III (D) II and IV

34. The molecules of mass m, moving with velocity v are absorbed after colliding with walls of a container. If the number of molecules per unit volume of the gas is N, then the pressure exerted by the gas will be
(A) $\frac{mNv^2}{2}$ (B) $2mNv^2$
(C) $\frac{mNv^2}{3}$ (D) mNv^2

35. For a real gas, pV is a constant over a small range of pressures at
(A) Boyle's temperature.
(B) critical temperature.
(C) inversion temperature.
(D) ordinary temperature.

36. The average, rms and most probable velocities of gas molecules at STP increase in the order

(A) rms < average velocity < most probable velocity
(B) Most probable velocity < average velocity < rms
(C) Average velocity < rms < most probable velocity
(D) rms < most probable velocity < average velocity

37. Which of the following statement is correct?

(A) The slope of Z vs. p at constant temperature for all real gases, is b/RT.
(B) The slope of Z vs. p at constant temperature for both He and H_2 is b/RT.
(C) The slope of Z vs. p at low pressure for all real gases, at constant temperature is b/RT.
(D) The slope of Z vs. p at high pressure and at constant temperature for real gas is $-b/RT$.

38. The density of the gaseous mixture (He and N_2) is 10/22.4 g L^{-1} at NTP. What is the percentage composition of He and N_2 by volume in this mixture, respectively?

(A) 75%, 25%
(B) 25%, 75%
(C) 30%, 70%
(D) 40%, 60%

39. Which of the following statement is (are) correct for a gas X having molar mass 5 g and density 0.3 g L^{-1} at 0.5 atm pressure at 300 K?

(A) The gas X will behave ideally.
(B) The force of attraction will dominate over the force of repulsion among the gas molecules.
(C) The force of repulsion will dominate over the force of attraction among the gas molecules.
(D) None of these.

40. At STP, a container has 1 mol of Ar, 2 mol of CO_2, 3 mol of O_2 and 4 mol of N_2. Without changing the total pressure if 1 mol of O_2 is removed, the partial pressure of O_2 is

(A) changed by about 26%.
(B) halved.
(C) unchanged.
(D) changed by 33%.

41. When 100 mL sample of methane and ethane along with excess of O_2 is subjected to electric spark, the contraction in volume was observed to be 212 mL. When the resulting gases were passed through KOH solution, further contraction in volume was

(A) 60 mL
(B) 96 mL
(C) 100 mL
(D) 112 mL

42. Under same conditions of temperature and pressure a hydrocarbon of molecular formula C_nH_{2n-2} was found to diffuse $3\sqrt{3}$ times slower than hydrogen. Find the value of n?

(A) $n = 2$
(B) $n = 4$
(C) $n = 3$
(D) $n = 1$

43. 5 mL of a gaseous hydrocarbon was exposed to 30 mL of O_2. The resultant gas, on cooling is found to measure 25 mL, of which 10 mL was absorbed by NaOH and the remainder by pyrogallol. All measurements are made at constant pressure and temperature. The molecular formula of the hydrocarbon is

(A) C_2H_2
(B) C_3H_8
(C) C_2H_4
(D) C_2H_6

44. A gas mixture of 3 L of propane (C_3H_8) and butane (C_4H_{10}) on complete combustion at 25°C produced 10 L CO_2. What is the composition of gas mixture, that is, volume of C_3H_8 and C_4H_{10}, respectively?

(A) 1.5 L, 1.5 L
(B) 1 L, 2 L
(C) 2 L, 1.0 L
(D) 1. 75 L, 1. 25 L

45. A vessel of volume 0.02 m^3 contains a mixture of hydrogen and helium at 20°C and 2 atm pressure. The mass of mixture is 5 g. Find the ratio of mass of hydrogen to that of helium in the mixture (atomic weight of He = 4 *u*.)

(A) 1:2
(B) 1:3
(C) 2:3
(D) 3:2

46. The average speed of an ideal gas molecule at 27°C is 0.3 m s^{-1}. Calculate average speed at 927°C?

(A) 0.6 m s^{-1}
(B) 6 m s^{-1}
(C) 60 m s^{-1}
(D) 8 m s^{-1}

47. The pressure–volume plot for an ideal gas at a given temperature has the form of a

(A) straight line.
(B) exponential curve.
(C) rectangular hyperbola.
(D) U-shaped curve.

48. If a graph is drawn for 1 mol real gas in such a way, pV is drawn in y-axis and p in x-axis then which of the following be the value for the intercept of the graph in y-axis.

(A) $RT + \dfrac{ab}{V^2} - aV$
(B) $RT + pb + a$
(C) $RT + pb + ab$
(D) RT

49. Joule–Thomson expansion of an ideal gas is an

(A) isothermal process.
(B) isobaric process.
(C) isoenthalpic process.
(D) ideal process.

50. There are 201 equidistant rows of spectators sitting in a hall. A magician releases laughing gas N_2O from the front and the tear gas ($M_o = 176$) from the rear of the hall simultaneously. Which row of spectators will have a tendency to smile and weep simultaneously?

(A) 130
(B) 134
(C) 120
(D) 100

51. The average kinetic energy of two moles of CO_2 at a certain temperature is 1800 cal. The temperature of the gas is

(A) 300 K
(B) 150 K
(C) 200 K
(D) 400 K

52. Equal volumes of SO_2 and He at a temperature T and pressure p are allowed to effuse through a hole. The rate of effusion of helium is

(A) equal to the rate of effusion of SO_2.
(B) four times the rate of effusion of SO_2.
(C) half of the rate of effusion of SO_2.
(D) twice the rate of effusion of SO_2.

53. At point A the gas is at Boyle's temperature and it is brought to B as shown in Fig. 3.45. Then at point B the gas will have compressibility factor
(A) 1
(B) $Z > 1$
(C) $Z < 1$
(D) $Z = 3/8$

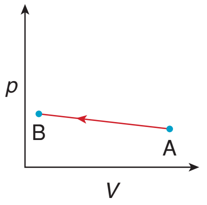


Figure 3.45

54. The van der Waals constants for a gas are: $a = 4$ L^2 atm mol^{-2}, $b = 0.04$ L mol^{-1}. Its Boyle temperature is roughly
(A) 100°C (B) 1220 K
(C) 1220°C (D) 1600 K

55. Oxygen is present in 1 L flask at a pressure of 7.6×10^{-10} mm Hg. Calculate the number of oxygen molecules in the flask at 0°C.
(A) 2.686×10^{10} (B) 26.86×10^{10}
(C) 0.626×10^{12} (D) 4.123×10^{8}

56. Pressure remaining the same, the volume of given mass of an ideal gas increases for every degree centigrade rise in temperature by definite fraction of its volume at
(A) 0°C. (B) its critical temperature.
(C) absolute zero. (D) its Boyle temperature.

57. 4.0 g of argon has pressure p atm at temperature T K in a vessel. On keeping the sample at 50° higher temperature, 0.8 g gas was given out to maintain the pressure p. The original temperature was
(A) 73 K (B) 100 K
(C) 200 K (D) 510 K

58. X mL of H_2 gas effused through a hole in a container in 5 s. The time taken for the effusion of the same volume of the gas specified below under identical conditions is
(A) 10 s:He (B) 20 s:O_2
(C) 25 s:CO (D) 55 s:CO_2

59. The rms velocity of hydrogen is $\sqrt{7}$ times the rms velocity of nitrogen. If T is temperature of the gas, then
(A) $T(H_2) = T(N_2)$ (B) $T(H_2) > T(N_2)$
(C) $T(H_2) < T(N_2)$ (D) $T(H_2) = \sqrt{7}\ T(N_2)$

60. Flask X is filled with 20 g of CH_4 gas at 100°C and another identical flask Y with 40 g O_2 gas at the same temperature. Which one of the following statements is correct? [Molar masses in g mol^{-1} of CH_4 = 16.0 and O_2 = 32.0]
(A) The pressure of the gases in the two flasks are identical.
(B) The pressure of CH_4 in flask X is higher than that of O_2 in flask Y.
(C) The pressure of CH_4 in flask X is lower than that of O_2 in flask Y.
(D) The pressure of CH_4 in flask X is half that of O_2 in flask Y.

61. What would be the S.I. unit for the quantity pV^2T^2/n?
(A) dm^5 Pa K^2 mol^{-1} (B) dm^3 Pa K^2 mol^{-1}
(C) dm^2 Pa^2 K^2 mol^{-1} (D) dm^6 Pa K mol^{-1}

62. At 0°C, the density of a certain gaseous oxide at 2 bar is same as that of dinitrogen at 5 bar. What is the molecular mass of the oxide?
(A) 70 g mol^{-1} (B) 35 g mol^{-1}
(C) 140 g mol^{-1} (D) None of these

63. 40.0 mL of a gaseous mixture of CO and C_2H_2 is mixed with 100.0 mL of O_2 and burnt. The volume of the gas after the combustion is 105 mL. Calculate the composition of the original mixture.
(A) 25 mL of CO and 15 mL of C_2H_2
(B) 15 mL of CO and 25 mL of C_2H_2
(C) 10 mL of CO and 30 mL of C_2H_2
(D) 20 mL of CO and 20 mL of C_2H_2

64. 380 mL of a gas at 27°C, 800 mm Hg weighs 0. 455 g. The molecular weight of gas in g mol^{-1} is
(A) 27 (B) 28
(C) 29 (D) 30

65. The rate of diffusion of O_2 and H_2 at same p and T are in the ratio
(A) 1:4 (B) 1:8
(C) 1:16 (D) 4:1

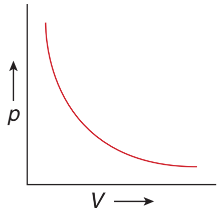
66. What will be the pressure exerted by a mixture of 3.2 g of methane and 4.4 g of carbon dioxide contained in 9 dm^3 flask at 27°C?
(A) 8. 314 Pa (B) 8.314×10^2 Pa
(C) 2×10^2 Pa (D) 8.314×10^4 Pa

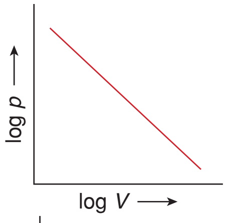
67. The average velocity of an ideal gas molecule at 27°C is 0.3 m s^{-1}. The average velocity at 927°C will be
(A) 0.6 m s^{-1} (B) 0.3 m s^{-1}
(C) 0.9 m s^{-1} (D) 3.0 m s^{-1}

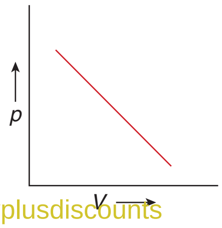
68. The root mean square velocity of an ideal gas at constant pressure varies with density as
(A) ρ^2 (B) ρ
(C) $\rho^{1/2}$ (D) $1/\rho^{1/2}$

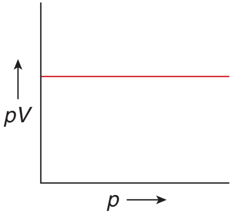
69. The values of van der Waals constant a for the gases O_2, N_2, NH_3, and CH_4 are 1.360, 1.390, 4.170 and 2.253 L^2 atm mol^{-2}, respectively. The gas which can most easily be liquefied is
(A) O_2 (B) N_2
(C) NH_3 (D) CH_4

70. Which curve does not represent Boyle's law?

(A)


(B)


(C)


(D)


71. The circulation of blood in human body supplies O_2 and releases CO_2. The concentration of O_2 and CO_2 is variable but on the average, 100 mL blood contains 0.02 g of O_2 and 0. 08 g of CO_2. The volume of O_2 and CO_2 at 1 atm and at body temperature of 37°C, assuming 10 L blood in human body, would be

(A) 2 L, 4 L (B) 1.5 L, 4.5 L
(C) 1.59 L, 4.62 L (D) 3.82 L, 4.62 L

72. In the graph shown in Fig. 3.46 of Maxwell–Boltzmann distribution of molecular velocities

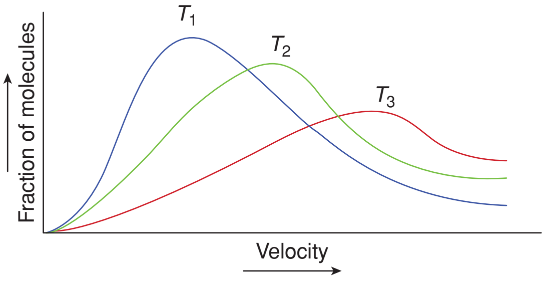


Figure 3.46

Which of the following is the correct order of temperature?

(A) $T_1 < T_2 < T_3$ (B) $T_3 < T_2 < T_1$
(C) $T_2 < T_1 < T_3$ (D) None of these

73. The vapor density of gas is 11.2. The volume occupied by 11.2 g of this gas at STP is

(A) 22.4 L (B) 11.2 L
(C) 1 L (D) 2. 24 L

74. NH_3 gas is liquefied more easily than N_2 thereby

(A) van der Waals constants a and b of NH_3 is higher than that of N_2
(B) van der Waals constant a and b of NH_3 is less than that of N_2
(C) a of NH_3 > a of N_2, but b of NH_3 < b of N_2
(D) a of NH_3 < a of N_2, but b of NH_3 > b of N_2

75. When 100 mL sample of methane and ethane along with excess of O_2 is subjected to electric spark, the contraction in volume was observed to be 212 mL. When the resulting gases were passed through KOH solution, further contraction in volume was:

(A) 60 mL (B) 96 mL
(C) 108 mL (D) None of these

76. At STP, a container has 1 mol of Ar, 2 mol of CO_2, 3 mol of O_2 and 4 mol of N_2. Without changing the total pressure if one mole of O_2 is removed, the partial pressure of O_2

(A) is changed by about 26%.
(B) is halved.
(C) is unchanged.
(D) changed by 33%.

77. The ratio, rms velocity of SO_2 to that of He at 30°C is equal to

(A) 4 (B) 0.25
(C) 0.10 (D) 8

78. Predict which of the following statements are true and which are false.

(I) For constant volume if temperature is increased pressure increases due to the increase in the number of collisions among the molecules.
(II) For a real gas at NTP if Z > 1 then $V_m < 22.4$ L.
(III) Gases can be solidified just below their critical temperature.

(A) T T T (B) T T F
(C) T F F (D) F F F

79. Choose the correct statement for viscosity (η) variation with T and p for an ideal gas.

(A) η of a gas increases with increase in temperature (T), but it is independent of pressure.
(B) η of a gas decreases with increase in T and increases with increase in p.
(C) η of a gas is independent of temperature and pressure.
(D) η of a gas increases with increase in both T and p.

80. What is the ratio of u_{rms}/u_{mp} for methane gas at 300K?

(A) 1.22 (B) 2.22
(C) 2.08 (D) 1.08

81. For a sample of gas X shown in Fig. 3.47, the rms velocity at temperature T will be

(A) 328 m s^{-1}
(B) $\sqrt{\dfrac{3\pi}{8}} \times 400$ m s^{-1}
(C) 490 m s^{-1}
(D) 400 m s^{-1}

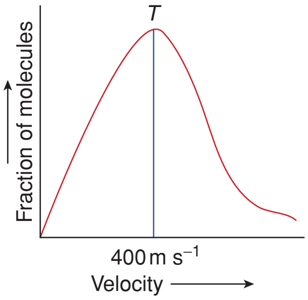


Figure 3.47

Multiple Correct Choice Type

1. Which of the following statements are correct?

(A) He diffuses at a rate of 8.65 times as much as CO does.
(B) He escapes at a rate of 2.65 times as much as CO does.
(C) He escapes at a rate of 4 times of as CO_2.
(D) He escapes at a rate of 4 times as fast as SO_2 does.

2. Select correct statements:

(A) Gases tend to behave non-ideally at low temperatures and high pressures.
(B) Gases tend to behave ideally at high temperatures and low pressures.
(C) The extent to which Z deviates from 1 is a measure of the non-ideality of a gas.
(D) $Z = 1$ under critical states.

3. Which of the following statements is/are wrong?

(A) At a given temperature the transitional K.E. of one mole of every gas is same which is equal to (3/2)RT.

(B) K.E. of a gas depends on its mass.
(C) K.E. depends on the volume.
(D) K.E. depends on the pressure.

4. What is the conclusion you would draw from the following graphs shown in Fig. 3.48?

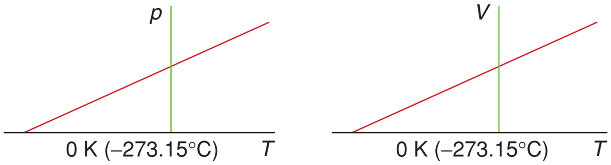


Figure 3.48

(A) As the temperature is reduced, the volume as well as the pressure increases.
(B) As the temperature is reduced, the volume becomes zero and the pressure reaches infinity.
(C) As the temperature is reduced, both the volume and the pressure decrease.
(D) A point is reached where theoretically, the volume as well as the pressure become zero.

5. Which of the following statements is wrong for gases?
(A) Gases do not have a definite shape and volume.
(B) Volume of the gas is equal to volume of container confining the gas.
(C) Confirmed gas exerts uniform pressure on the walls of its container in all directions.
(D) Mass of gas cannot be determined by weighing a container in which it is enclosed.

6. A gas described by van der Waals equation:
(A) behaves similar to an ideal gas in the limit of larger molar volumes.
(B) behaves similar to an ideal gas in the limit of large pressures.
(C) is characterized by van der Waals coefficients that are dependent on the identity of the gas but are independent of the temperature.
(D) has the pressure that is lower than the pressure exerted by the same gas behaving ideally.

7. According to kinetic theory of gases.
(A) Pressure of the gas molecule is proportional to most probable speed of the gas molecules.
(B) The pressure exerted by the gas molecule is proportional to root mean square speed of the gas molecules.
(C) The root mean square speed is directly proportional to square root of the Kelvin temperature.
(D) Kinetic energy of the gas molecules does not depend upon, p, V and molar mass of the gas molecules.

8. Consider a sample of equimolar mixture of He gas and No gas both at 300 K and 1 atm. Assuming ideal gas behavior which of the following quantities are equal for two samples?
(A) Root mean square speed of molecules
(B) Mean translational kinetic energy of molecules
(C) Number density of molecules
(D) Kinetic energy of molecules

9. Consider the following statements:
(A) Atmospheric pressure is less at the top of a mountain than at sea level.
(B) Gases are much more compressible than solids or liquids.
(C) When the atmospheric pressure increases, the height of the mercury column rises.
(D) Both c and d.

10. For an ideal gas, under isobaric condition, a graph between log V vs. log T:
(A) is linear with unit slope.
(B) represents Boyle's law.
(C) represents Charle's law.
(D) represents Gay–Lussac's law.

11. A mixture of O_2 and He kept in a container at 27°C. Which of the following statements are correct?
(A) O_2 molecule will hit the wall of the container with smaller average speed as compared to He.
(B) O_2 molecules will hit the wall of the container with greater average speed as compared to He.
(C) O_2 molecule will hit the wall of the container with the greater kinetic energy as compared to He.
(D) O_2 molecule will hit the wall the container with equal kinetic energy as compare to He.

12. Which of the following are correct statements?
(A) van der Waals constant a is a measure of attractive force.
(B) van der Waals constant b is also called co-volume or excluded volume.
(C) b is expressed in L mol^{-1}.
(D) b is one-third of critical volume.

13. H_2 and N_2 are contained in two separate isothermal vessels connected by a thin tube. When the valve separating the two vessels is opened, which of the following will be true for the final state? Both the vessels are at same temperature
(A) Mass of H_2 in vessel A = Mass of H_2 in vessel B
(B) Mass of N_2 in vessel A = Mass of N_2 in vessel B
(C) Mass of H_2 in vessel A = Mass of N_2 in vessel A
(D) Total pressure will be same in vessels A and B

Assertion–Reasoning Type

Choose the correct option from the following:
(A) **Statement 1** is True, Statement 2 is True; Statement 2 is a correct explanation for Statement 1.
(B) **Statement 1** is True Statement 2 is True; Statement 2 is NOT a correct explanation for Statement 1.
(C) **Statement 1** is True, Statement 2 is False.
(D) **Statement 1** is False, Statement 2 is True.

1. **Statement 1:** One mole of helium atoms should occupy 22.4 L volume at STP.

Statement 2: Taking 31 pm as radius of helium atoms, if we pack together a mole of helium atoms, the mole of atoms should have a volume of 22.4 L.

2. **Statement 1:** At low pressure van der Waals equation is reduced to $\left(p+\frac{a}{V^2}\right)V = RT$

Statement 2: The compressibility factor corresponding to low pressure is given by $1-\frac{RTV}{a}$.

3. **Statement 1:** A sample of 8.00 mol of chlorine gas in 94.00 L tank at 27°C leads to a pressure of 2.096 atm according to ideal gas law.

Statement 2: The actual pressure of the sample of chlorine is nearly 20 atm less than the ideal pressure.

4. **Statement 1:** The value of the van der Waals constant a is large for NH_3 than PH_3.

Statement 2: Hydrogen bonding is present in NH_3.

5. **Statement 1:** Absolute zero is lowest possible temperature.

Statement 2: A lower temperature than absolute zero would correspond to negative value of volume of gas which is meaningless.

6. **Statement 1:** Equal volumes of all gases under similar conditions of temperature and pressure contain equal number of molecules.

Statement 2: Volume of a gas is inversely proportional to pressure.

7. **Statement 1:** Compressibility factor for hydrogen varies with pressure with positive slope at all pressures.

Statement 2: Even at low pressures, repulsive forces dominate hydrogen gas.

Comprehension Type

Read the paragraphs and answer the questions that follow.

Paragraph I

The real gases deviate from ideal behavior due to the following reasons:

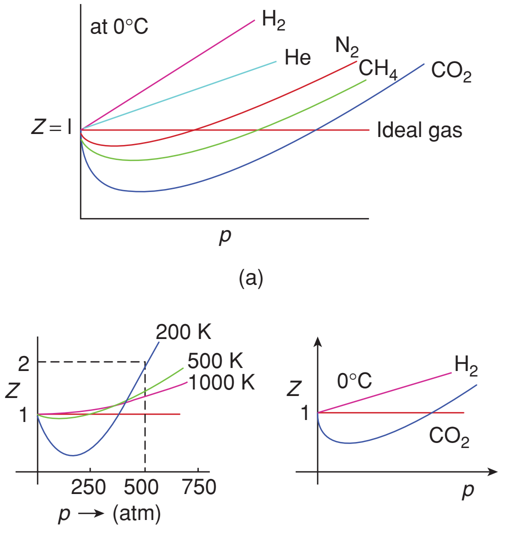
(a) The actual volume occupied by the gas molecule is negligible as compared to the total volume of the gases.

(b) The forces of attraction and repulsion among the gas molecules are negligible.

The extent of deviation of the real gas from ideal behavior is explained by compressibility factor (Z), which is function of pressure and temperature for real gas.

For ideal gas, $Z = 1$ whereas for real gases two cases arise. When $Z > 1$, which means it is less compressible because force of repulsion dominates over force of attraction. When $Z < 1$, the force of attraction dominates over the force repulsion.

The graph of Z vs. p for different gases at one temperature is shown in Fig. 3.49(a), and the graph of Z vs. p for 1 mol of hypothetical gas at three distinct temperature temperatures is shown in Fig. 3.49(b).



(a)

(b)

Figure 3.49

Boyle's temperature $T_B = a/Rb$ is the temperature at which a gas shows ideal behavior over a pressure range in the low pressure region. If a plot is obtained at temperature well below Boyle's temperature than the curve will show negative deviation, in low pressure region and positive deviation in the high pressure region. Near critical temperature the curve is more likely as CO_2 and the temperature well above critical temperature curve is more like H_2 at (0°C) as show above. At high pressure suppose all the constant temperature curve varies linearly with pressure according to the following equation:

$$Z = 1+\frac{pb}{RT}\ (R = \text{cal mol}^{-1}\text{K}^{-1})$$

The van der Waal's equation of state for 1 mole of gas is as under:

$$\left(p+\frac{a}{V^2}\right)(V-b) = RT \qquad (1)$$

where a and b are van der Waal s constants. The van der Waals constant a measures the amount of the force of attraction among the gas molecules. Higher the value of a, higher will be the ease of liquefaction.

When pressure is too high like in case of H_2 and He, the equation will reduce to $p(V-b) = RT$.

When pressure is too low like in case of N_2, CH_4 or CO_2, the equation will reduce to $\left(p+\frac{a}{V^2}\right)V = RT$.

1. What is the correct increasing order of a of the gases shown as in Fig. 3.42(b)?

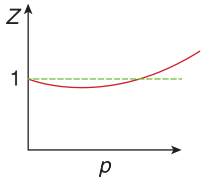
(A) $H_2 < He < N_2 < CO_2$ (B) $CO_2 < N_2 < He < H_2$
(C) $N_2 < CO_2 < H_2 < He$ (D) $N_2 < H_2 < He < CO_2$

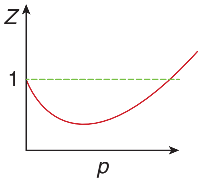
2. Which of the following is correct?
(A) $(a/b) < 0.4$ cal mol^{-1}
(B) 0.4 kcal mol^{-1} $< (a/b) < 2$ kcal mol^{-1}
(C) $(a/b) > 0.4$ kcal mol^{-1}
(D) $(a/b) = 1$ kcal mol^{-1}

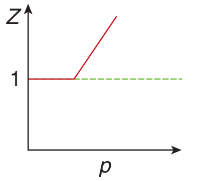
3. For 500 K, the plot the value of Z changes from 2 to 2. 2. If pressure is varied from 100 atm to 1200 atm (high pressure) then the value of b/RT will be:
(A) 10^{-3} atm^{-1} (B) 2×10^{-3} atm^{-1}
(C) 5×10^{-4} atm^{-1} (D) 10^{-4} atm^{-1}

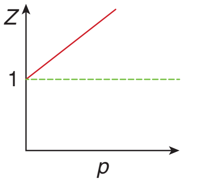
4. As shown in Fig. 3.49(a) at 200 K and 500 atm value of compressibility factor is 2 (approx.). Then volume of the gas at this point will be:
(A) 0. 01 L (B) 0. 09 L
(C) 0. 065 L (D) 0. 657 L

5. Plot at Boyle's temperature for the gas will be:

(A)


(B)


(C)


(D)


6. Which of the following is the correct increasing order of temperature? For a given gas as shown in Fig. 3.49(b),
(A) $T_1 < T_2 < T_3 < T_4$ (B) $T_2 < T_1 < T_3 < T_4$
(C) $T_3 < T_4 < T_1 < T_2$ (D) $T_4 < T_3 < T_2 < T_1$

Paragraph II

Gas molecules are in a constant state of motion, thus colliding with each other and with the wall of container. Maxwell and Boltzmann proposed due to such collisions, the velocities of gas molecules are always variable. A fraction of molecules can be considered to have a particular molecular velocity at a time. Maxwell calculated the distribution of velocity among fraction of total number of molecules based on probability. The average, most probable and root mean square velocities of the fraction of gas molecules are expressed as

$$u_{\text{avg}} = \sqrt{\frac{8RT}{\pi M}} \quad u_{\text{mp}} = \sqrt{\frac{2RT}{M}} \quad u_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

7. The ratio $u_{\text{rms}}:u_{\text{avg}}:u_{\text{mp}}$ is
(A) $1:0.921:0.816$ (B) $2:0.0921:1$
(C) $3:0.0921:8$ (D) $4:0.0921:0816$

8. Calculate rms speed of O_2 molecules having K.E. of 2 kcal mol^{-1}
(A) 22. 795 m s^{-1} (B) 30 m s^{-1}
(C) 32 m s^{-1} (D) 52 m s^{-1}

Paragraph III

For 1 mol of gas, the van der Waals equation is

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT$$

where a signifies the force of attraction among the gas molecules and b signifies the incompressible volume, that is, the volume having no effect of compression and expansion. The compressible volume, that is the volume having effect of compression and expansion $= V - b$ for 1 mol real gas. Another form of van der Waals equation of states is called virial equation. The virial equation for 1 mol real gas is

$$\frac{pV_\text{m}}{RT} = 1 + \frac{B}{V_\text{m}} + \frac{C}{V_\text{m}^2} + \ldots \text{ to higher powers of } n$$

where B and C are known as first and second virial coefficients, respectively. The temperature at which real gases obey ideal gas equation is $PV = RT$, is known as Boyles temperature, T_B.

9. If the second virial coefficient of 3 mol of He at NTP be 6.4×10^{-2} (L mol^{-1})^3, then what will be the real volume of He gas?
(A) 66.0 L (B) 23.6 L
(C) 25 L (D) 68.4 L

10. Which of the following is the correct statement about the Boyle's temperature (T_B)?
(A) The temperature at which second virial coefficient becomes zero.
(B) The temperature at which first virial coefficient is zero.
(C) The value of T_B is $2a/Rb$.
(D) None of these

11. For the constant value of b, if the Boyle's temperature of the gases is increased, then what will be the effect on the ease of liquefication?
(A) It will increase, on increasing the Boyle's temperature.
(B) It will decrease, on increasing the Boyle's temperature.
(C) First liquidation will increase, then it will decrease.
(D) No effect

Integer Answer Type

The answer is a **non-negative integer**.

1. The stop cock connecting two bulbs of volume 5 and 10 L containing an ideal gas at 9 and 6 atm, respectively, is opened. The final pressure (in atmosphere) in the two bulbs if the temperature remains the same is __________.

2. A compound exists in the gaseous phase both as monomer (A) and dimer (A_2). The molecular weight of A is 48. In an experiment 96 g of compound was confined in vessel of volume 33.6 L and heated to 273°C. Calculate the pressure developed if the compound exists as dimer to the extent of 50% by weight under these conditions.

3. If the pressure and absolute temperature of 2 L of carbon dioxide are doubled, the volume (in liter) of carbon dioxide would become __________.

4. 4 g of an ideal gas was introduced into a bulb of volume of 0. 821 dm^3 at certain pressure, P and temperature T, The above bulb was placed in a thermostat mentioned at temperature (T + 125)K of 0.8 g of the gas was left off to keep the original pressure. Calculate the pressure in atmosphere. [Molecular weight of the gas is 40 g mol^{-1} and R value is 0. 0821 L atm K^{-1} mol^{-1}.]

5. One mole of an ideal monoatomic gas is mixed with one mole of an ideal diatomic gas. The molar specific heat (in calories) of the mixture at constant volume is __________.

6. If the slope of Z (compressibility factor) vs. p curve is constant (slope = 492.6 atm^{-1}) at a particular temperature (300 K) and very high pressure then the diameter of the molecules is __________. (Given $N_A = 6.0 \times 10^{23}$, $R = 0.0821$ atm L mol^{-1} K^{-1}.)

Matrix–Match Type

1. Match the term with its expression.

Column I	Column II
(A) RMS velocity	(p) $\sqrt{\frac{8RT}{\pi M}}$
(B) Average velocity	(q) $\frac{1}{3}\frac{mNu^2}{V}$
(C) Most probable velocity	(r) $\sqrt{\frac{3RT}{M}}$
(D) Pressure by kinetic theory of gases	(s) $\sqrt{\frac{2RT}{M}}$
	(t) $\sqrt{\frac{2p}{\rho}}$

(Continued)

2. Match the expression with the type of changes it undergoes.

Column I	Column II
(A) $p = 2V^2$	(p) If volume increases the temperature will also increase.
(B) pV^2 = constant	(q) If volume increases the temperature will decrease.
(C) $C = C_V + 2R$	(r) For expansion, heat will have to be supplied to the gas.
(D) $C = C_V - 2R$	(s) If temperature increases then work done by gas is positive.

3. Match the compression factor under different conditions with its value.

Column I	Column II
(A) Compression factor (Z) for ideal gas	(p) 3/8
(B) Z for real gas at low pressure	(q) $(1 + pb)/RT$
(C) Z for real gas at high pressure	(r) 1
(D) Z for critical state	(s) $(1 - a/RTV)$
	(t) pV/nRT

ANSWERS

Review Questions

1. 0.6 atm
2. 1.3 L
3. Eight
4. **(a)** Charles's law
  (b) Gay–Lussac's law
  (c) Avogadro's law;
  (d) Combined gas law
5. Ethanol and sulphur dioxide
6. H_2
10. 250 mL
14. 1.004:1
17. 1:1
18. For monoatomic gases
19. NH_3
20. No

Numerical Problems

1. 12.04×10^{23} molecules; 5.313×10^{-23} g
2. 9.33 atm
3. 0.2 atm
4. 36.36 g
5. 9.43s
6. 2.24
7. **(a)** No; **(b)** 34.75 K
8. $\%CO_2 = 60\%$ and $\%CO = 40\%$
9. $\%O_2 = 47.16\%$ and $\%CO_2 = 52.83\%$
10. **(a)** 9.84 atm; **(b)** 9.32 atm
11. **(a)** **(i)** 18. 09; **(ii)** 50.25 L; **(iii)** 1.224 L; **(iv)** $Z > 1$; the repulsive force will dominate
  (b) 2.07×10^{-20} J per molecule
12. $Z = 0.6496$
13. **(a)** 490.5 mm Hg;
  (b) 259.5 mm Hg

14. 4 atm
15. 566 K
16. **(a)** 44.82 mL; **(b)** 8.98 mL
17. $\%N_2 = 82.44\%$ and $\%O_2 = 17.5\%$
18. $\%CH_4 = 65\%$ and $\%C_2H_2 = 35\%$
19. 17.87 dm^3
20. 0.4; 2.4×10^{23}; 0.8 g
21. 14.439 kg
22. $u_{rms} = 45.80$ m s^{-1}; $u_{avg} = 42.16$ m s^{-1}; $u_{mp} = 37.39$ m s^{-1}
23. 0.036 atm; 0.004 L
24. **(a)** 4; **(b)** 1200 K; **(c)** No effect; **(d)** No effect
25. 0.4; 0.6; 300 mm Hg
26. 1256.93°C
27. C_2H_2
28. 50% increase
29. 3.8×10^{13}
30. 0.964:1
31. **(a)** 591.01 mL; **(b)** 278.63 mL; **(c)** 1.67 atm; **(d)** 0.833 atm; **(e)** 22.4 L
32. 3.72 cm^3 $molecule^{-1}$ 41.4×10^{-8} cm

Additional Objective Questions

Single Correct Choice Type

1. (B)
2. (C)
3. (B)
4. (B)
5. (A)
6. (C)
7. (A)
8. (D)
9. (C)
10. (C)
11. (C)
12. (A)
13. (B)
14. (D)
15. (D)
16. (A)
17. (C)
18. (A)
19. (D)
20. (B)
21. (D)
22. (B)
23. (D)
24. (B)
25. (C)
26. (A)
27. (C)
28. (A)
29. (A)
30. (D)
31. (A)
32. (C)
33. (D)
34. (D)
35. (A)
36. (B)
37. (B)
38. (A)
39. (B)
40. (A)
41. (D)
42. (B)
43. (C)
44. (C)
45. (A)
46. (A)
47. (C)
48. (D)
49. (C)
50. (B)
51. (A)
52. (B)
53. (C)
54. (B)
55. (A)
56. (A)
57. (C)
58. (B)
59. (C)
60. (A)
61. (A)
62. (A)
63. (A)
64. (B)
65. (A)
66. (D)
67. (A)
68. (D)
69. (C)
70. (C)
71. (C)
72. (A)
73. (B)
74. (C)
75. (D)
76. (A)
77. (A)
78. (C)
79. (A)
80. (A)
81. (C)

Multiple Correct Choice Type

1. (B, D)
2. (A, B, C)
3. (C, D)
4. (C, D)
5. (A, C)
6. (A, C, D)
7. (B, C, D)
8. (B, C, D)
9. (A, B)
10. (A, C)
11. (A, D)
12. (A, B, C, D)
13. (A, B, D)

Assertion–Reasoning Type

1. (C)
2. (C)
3. (B)
4. (A)
5. (A)
6. (A)
7. (A)

Comprehension Type

1. (A)
2. (D)
3. (A)
4. (C)
5. (A)
6. (D)
7. (A)
8. (A)
9. (D)
10. (A)
11. (A)

Integer Answer Type

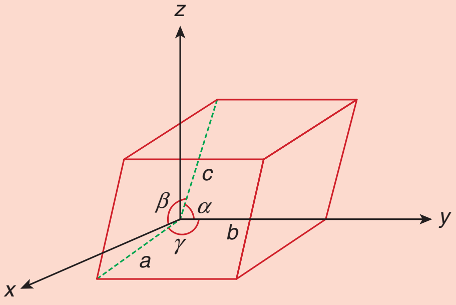
1. (7)
2. (2)
3. (2)
4. (5)
5. (4)
6. (5)

Matrix–Match Type

1. A → (r); B → (p); C → (s, t); D → (q)
2. A → (p, r, s); B → (q, r); C → (q); D → (p, r, s)
3. A → (r, t); B → (s, t); C → (q, r); D → (p, t)

4

Solid State



Representation of a unit cell

Contents

4.1 Classification of Solids
4.2 Crystal Lattices and Unit Cells
4.3 Calculations Involving Unit Cell Dimensions
4.4 Cubic Lattice – Simple, Face Centered and Body Centered
4.5 Close-Packing in Crystals
4.6 Packing Efficiency and Packing Fraction
4.7 Tetrahedral and Octahedral Voids
4.8 Radius Ratio Rule and Ionic Radius
4.9 Simple Ionic Compounds
4.10 X-Ray Diffraction Used to Study Crystal Structures (Bragg's Law)
4.11 Defects in Crystals
4.12 Electrical Properties of Solids
4.13 Magnetic Properties of Solids
4.14 Dielectric Properties of Solids

The solid state is characterized by its rigid form and tendency to maintain a definite shape. The constituent particles (atoms, molecules or ions) in a solid are held together by strong intermolecular, interatomic or interionic forces. The extent of binding forces between these particles determines the structure and properties of solids. The uses of solids are varied depending upon their characteristic properties such as melting points, electrical and magnetic properties; constituent particles and binding forces holding the particles together. For this purpose, the study of structure of solids is important to understand their use as superconductors, surgical instruments, polymers, packaging materials, etc.

The state in which the matter will exist is determined by the net effect of these two opposing forces. At low enough temperatures, the thermal energy of particles is low and the intermolecular distant between particles is less and the intermolecular forces of attraction are more, so the material exists as a solid. Most of the properties of the solid state are obvious to us. Still, it is worthwhile to note these common properties in order to visualize the actions and interactions of the ions or molecules that comprise these states. The properties of solids are as follows: They have **high density**; are **essentially incompressible**; undergo **little thermal expansion**; have a **fixed volume**, **mass and shape**; have **strong intermolecular forces** and therefore **more rigid**.

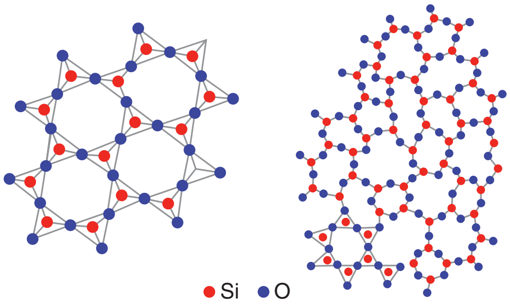
4.1 | CLASSIFICATION OF SOLIDS

Solids can be classified based on arrangement of particles into amorphous and crystalline solids; and based on the nature of bonds, they can be classified into molecular, ionic, metallic and covalent (network) solids. These are discussed in the following subsections.

Based on Arrangement of Particles

Solid state of matter is characterized by the rigidity of form and tendency to maintain a definite shape. In solids, the particles are packed in an orderly manner and can be divided into two distinct classes:

1. **Crystalline solids:** These consist of large number of crystals each of which has well-defined regular shape such as a cube, octahedron or tetrahedron. Crystals in general tend to have flat surfaces that meet at angles that are characteristic of the substance. The regularity of these surface features reflects the high degree of order among the particles (atoms, molecules, or ions) that lie within the crystal. For example, in crystals of sodium chloride – ordinary table salt, each particle is very nearly a perfect little cube. Whenever a solution of NaCl is evaporated, the crystals that form have edges that intersect at 90° angles. Crystalline solids are fairly widespread in nature. Metallic elements like copper, silver, non-metallic elements like sulphur and iodine and most of the ionic compounds such as sodium chloride, potassium nitrate are crystalline solids. Organic compounds such as benzoic acid, naphthalene, etc., are also crystalline.
2. **Amorphous solids:** These do not have a definite geometrical shape are known as amorphous solids. The word *amorphous* is derived from the Greek word *amorphos*, which means "without form". Amorphous solids do not have the kinds of long-range repetitive internal structures that are found in crystals. In some ways their structures, being jumbled, are more like liquids than solids. Like liquids, these solids also have a tendency to flow, though at a much slower rate. These are formed by sudden cooling of a liquid and are also sometimes called **supercooled liquids** or **pseudo solids**. For example, coal, coke, glass, plastic, rubber, sodium chloride and quartz glass, etc. In fact, the word **glass** is often used as a general term to refer to any amorphous solid.



Quartz (crystalline)

Quartz glass (amorphous)

Figure 4.1 Quartz in crystalline and amorphous forms.

It is difficult to make a distinction between truly amorphous solids and crystalline solids if the size of the crystal is very small. Even amorphous materials have some short-range order at the atomic length scale due the nature of chemical bonding. Amorphous solids soften on heating over a range of temperature and become crystalline at some temperature. For example, quartz exists in crystalline form and in amorphous form as quartz glass (Fig. 4.1).

The differences between the two are tabulated Table 4.1.

Table 4.1 Difference between amorphous and crystalline solids

Crystalline solids	Amorphous solids
The arrangement of atoms shows long-range three-dimensional order.	They do not show any long-range order.
They possess sharp melting points.	They melt over a wide range of temperature.
They show **anisotropy**.	They show isotropy.
They are cut along specific crystal planes.	They are cut along random directions and have irregular surfaces.
They have characteristic heat of fusion.	They do not have definite heat of fusion.
For example, metals, copper sulphate, $NiSO_4$, diamond, graphite, NaCl, sugar, etc.	For example, coal, coke, glass, plastic, rubber, sodium chloride and quartz glass, etc.

Note: Anisotropy is the property by which the magnitude of physical properties such as refractive index, thermal conductivity, etc., shows a variation with the direction in which it is measured. Isotropy is the property by which the substances exhibit the same values of any physical property in all directions.

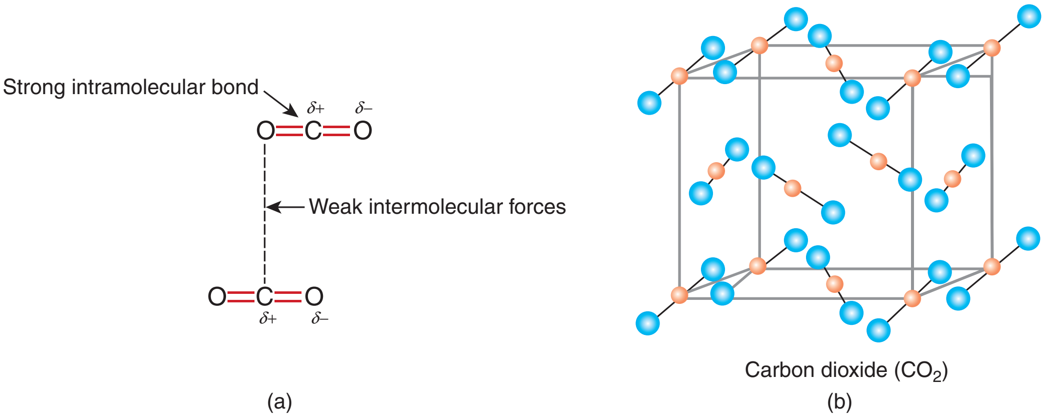
Many solids, such as aluminum and steel, have a structure that falls between the two extremes of Amorphous and Crystalline solids. Such **polycrystalline solids** are aggregates of large numbers of small crystals or grains within which the structure is regular, but the crystals or grains are arranged in a random fashion.

Based on Nature of Bonds

Crystalline solids may be classified into four categories based on the nature of intermolecular forces operating between the constituent particles. These are molecular, ionic, metallic (atomic) and covalent solids.

Molecular Solids

In these solids, the constituent particles are molecules. Molecular solids contain both *intramolecular* bonds and *intermolecular* forces [Fig. 4.2(a)]. The atoms within the individual molecules are held together by relatively strong intramolecular covalent bonds compared to the molecules in a molecular solid. Because the forces between these molecules are relatively weak, molecular solids are often soft substances with low melting points. For example, dry ice (solid CO_2) [Fig. 4.2(b)]. Other examples are iodine (I_2), cane sugar ($C_{12}H_{22}O_{11}$) and polyethylene. Water and bromine are liquids that form molecular solids when cooled slightly; F_2 freezes to form a molecular solid at –220°C.



(a) (b)

Figure 4.2 (a) Intramolecular and intermolecular binding forces in CO_2. (b) Structure of dry ice.

Note: Polyethylene $(–CH_2–CH_2–)_n$ is a soft plastic that melts at relatively low temperatures and is used for making carry bags. Replacing one of the hydrogens on every other carbon atom with a chlorine atom produces a plastic known as poly(vinyl chloride), or PVC, which is hard enough to be used for making plastic pipes, which are slowly replacing metal pipes for plumbing.

The strength of PVC can be attributed to the van der Waals force of attraction between the chains of $(–CH_2–CHCl–)_n$ molecules that form the solid.

Molecular solids are further classified into the following categories:

1. **Non-polar molecular solids:** These are molecular solids that comprise atoms such are argon or helium or molecules formed by non-polar covalent bonds such as the family of halogens, F_2, Cl_2, Br_2 and I_2. These molecules are held together by weak dispersion forces or London forces. They have low melting points and usually exist as liquids or gases at normal temperature and pressure conditions. They are soft and do not conduct electricity.
2. **Polar molecular solids:** These are covalent molecules with a dipole moment, such as HCl and HBr, also form molecular solids when cooled. Polar molecules have dipole–dipole interactions which hold the molecules together. This force controls the orientation of the HCl and HBr molecules as they pack as tightly as possible, in a manner that the negative end of one dipole is oriented towards the positive end of the other. These solids are also non-conducting and soft. They have melting points higher than those of non-polar molecular solids but are generally gases or liquids at room temperature.
3. **Hydrogen-bonded molecular solids:** These are molecular solids that contain polar covalent bonds in which one of the elements is hydrogen. The individual H_2O molecules in the molecular solid such as ice are held

together by a combination of dipole, dispersion and strong hydrogen-bond forces. These molecular solids generally exist as liquids or soft solids at room temperature and pressure conditions, and are non-conductors of electricity.

The individual molecules in the molecular solid are held together by a combination of dipole, dispersion and hydrogen-bond forces. The impact of these intermolecular forces is observed as an effect on the melting point of the compound and the enthalpy of fusion, ΔH_{fus}. Consider the following examples:

1. In halogens, the molecules are held together by dispersion forces. These forces depend on the number of electrons in the atoms or molecules, so as the size of the halogen atoms increases, the dispersion force interactions become stronger so both the melting point and the enthalpy of fusion increase with increasing molecular weight.
2. The effect of adding dipole–dipole and hydrogen-bond interactions to the intermolecular forces that hold molecules together can be seen with CH_3OCH_3, CH_3OH and H_2O. Two of the compounds, H_2O and CH_3OH, also form hydrogen bonds in addition to presence of dispersion and dipole forces. As the number of hydrogen atoms that can form hydrogen bonds increases from zero (CH_3OCH_3) and one per molecule (CH_3OH) to two per molecule (H_2O), there is a significant increase in the melting point.

The number of electrons, and hence the polarizability, of the compounds decreases as $CH_3OCH_3 < CH_3OH < H_2O$; and it might be expected that water would have the smallest enthalpy of fusion. The fact that water has the highest enthalpy of fusion shows the relative importance of hydrogen bonding.

Ionic Solids

In ionic solids, the constituent particles are ions. These solids are generally salts, such as NaCl, that form an extended three-dimensional network of ions held together by the strong force of attraction between ions of opposite charge. Ionic compounds form solids in which the force of attraction between the ions of opposite charge is maximized by keeping the ions as close together as possible. Since the force of attraction is inversely proportional to the square of the distance between the positive and negative charges, the strength of an ionic bond is also inversely proportional to the size of the ions that form the solid.

$$F = \frac{q_1 \times q_2}{r^2}$$

When the ions are large, the bond is relatively weak. However, the ionic bond is still strong enough to ensure that salts have relatively high melting and boiling points. For example, NaCl melts at 801°C and boils at 1413°C. These solids do not conduct electricity in solid state because the ions are held together by strong electrostatic forces. However, in the molten state or in aqueous solutions, these ions become free to move and conduct electricity.

Metallic Solids

Metallic solids hold metals together and are composed of positively charged metal cations in a three-dimensional array. Electrons in the valence shell of a metal atom are shared by many atoms, instead of just two. In effect, the valence electrons are *delocalized* over many metal atoms (Fig. 4.3). This means that the electrons are not confined to the space between nuclei of atoms. Since the electrons are not tightly bound to individual atoms, they are free to migrate through the metal. The metal cations are surrounded by a sea of delocalized electrons that form metallic bonds. Each metal atom contributes one or more electrons towards the sea of mobile electrons. In a metal, each atom is surrounded by as many neighboring atoms as possible. Lithium, for example, crystallizes in a structure where each atom touches eight nearest neighbors. The distance between the nuclei of the atoms is 0.304 nm.

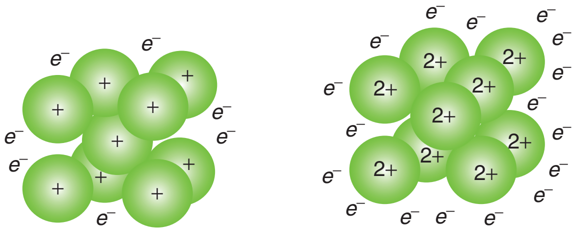


Figure 4.3 Sea of electrons in a metal.

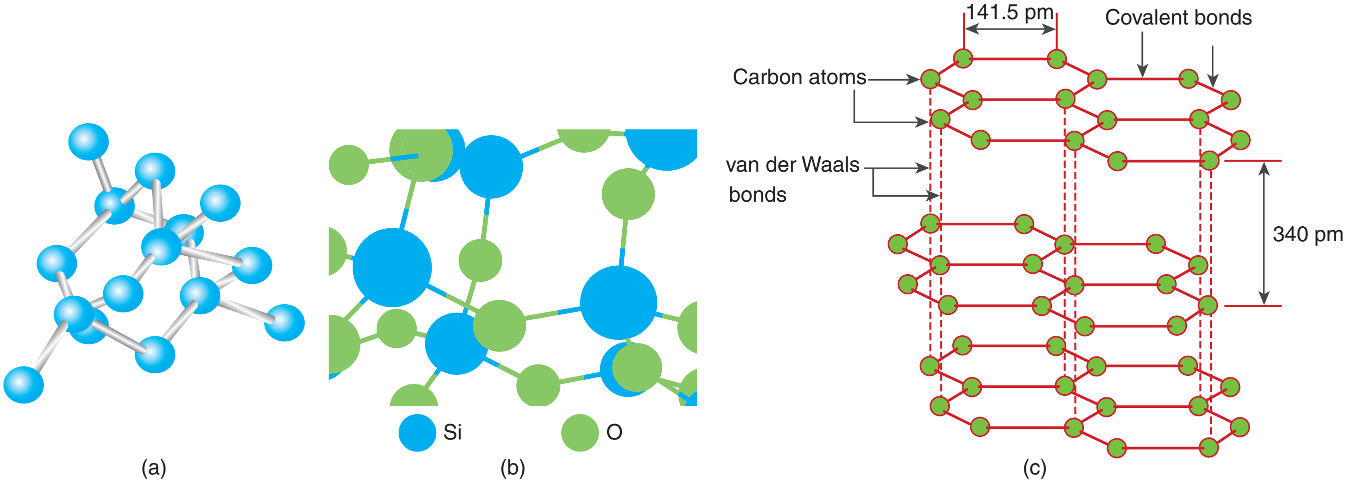
The properties of metallic solids are as follows:

1. Unlike ionic solids, metallic solids show high thermal and electrical conductivities due to the presence of these free electrons. When an electric current is applied to metallic solids, the sea of electrons begins to flow through the network of positive ions and conduct electricity. Similarly, when a portion of metal is heated, the free electrons of that zone gain thermal energy and transfer that energy to the adjoining electrons along the metal network. The thermal energy thus gets uniformly distributed, heating up the other portions of the solid.
2. Metallic solids have a wide range of melting points compared to ionic solids, which have higher melting points.
3. All metals, except for a few like alkali and alkaline earth metals, are malleable and ductile.
4. All metals possess luster and some of them are colored.

Covalent Network Solids

In covalent network solids, the atoms or chemical subunits are bonded by conventional covalent bonds in a continuous network. The bonding between chemical subunits is also identical to that within the subunits, resulting in a continuous network of chemical bonds. These are also called giant molecules because there are no individual molecules and the entire crystal may be considered as a macromolecule. Two common examples of network solids are diamond (a form of pure carbon, an atom) and quartz (silicon dioxide, a chemical subunit).

In diamond, each carbon atom is covalently bound to four other carbon atoms oriented towards the corners of a tetrahedron, as shown in Fig. 4.4(a). So diamond crystal can be viewed as a single giant molecule. Since all of the bonds in the structure are equally strong, diamond is the hardest natural substance, and it melts at 3550°C. In quartz, individual SiO_2 molecules cannot be identified; instead the solid is an extended three-dimensional network of –Si–O–Si–O– bonds as shown in Fig. 4.4(b).



(a) (b) (c)

Figure 4.4 Three-dimensional network of (a) diamond and (b) quartz. (c) Two-dimensional network of graphite.

Note: Graphite and the mica group of silicate minerals are also examples of covalent network solids. However, structurally they consist of continuous two-dimensional networks of covalently bonded atoms or chemical subunits. The two-dimensional layers are held together by van der Waals forces of attraction. Graphite consists of extended planes of carbon atoms in which each carbon forms strong covalent bonds to three other carbon atoms.

(a) The strong bonds between carbon atoms within each plane explain the exceptionally high melting and boiling points of graphite.

(b) The relatively weak van der Waals forces between the plane of atoms makes it easy to deform the solid by allowing one plane of atoms to slide over the other. Graphite is, therefore, soft enough to be used in pencils and as solid lubricant.

(c) Since each atom of carbon forms three covalent bonds with the neighboring carbon atoms in the same layer, the fourth valence electron of each carbon atom is delocalized and free to move about. These free electrons are responsible for electrical conductivity of graphite [Fig. 4.4(c)].

The formulas of covalent network solids are simple ratios of the component atoms represented by a single formula unit. The covalent bonds between the atoms or chemical subunits are very strong and directional. Hence, these solids are very hard and brittle, and have high melting points. However, they do not conduct electricity in solid state as there are no free electrons. Unlike ionic compounds, they do not conduct electricity in molten state because of absence of ions.

The different properties of the four types of crystalline solids are given in Table 4.2.

Table 4.2 Types of solids and their properties

Type of solid	Nature of constituent particles	Nature of interaction between particles	Physical and electrical properties	Examples
Molecular:	Molecules			
(a) Non-polar		(a) Dispersion or London forces	(a) Soft	(a) H_2, CO_2
(b) Polar		(b) Dipole–dipole force	(b) Low melting points	(b) HCl, SO_2
(c) Hydrogen bonded		(c) Hydrogen bonding	(c) Non-conductors of electricity in both solid and liquid states	(c) H_2O
Ionic	Ions	Ionic (Coulombic or electrostatic) bonding	(a) Relatively hard (b) Brittle (c) High melting points (d) Non-conductors of electricity as solids, but conduct when melted	NaCl, MgO, ZnS
Metallic	Positive metal ions in a sea of delocalized "free electrons"	Metallic bonding	(a) Range from very hard to very soft (b) Melting points range from high to low (c) Conduct electricity in both solid and liquid states (d) Have characteristic luster	Fe, Mg, Cu
Network	Atoms and chemical subunits	Covalent bonding	(a) Very hard (b) Very high melting points (c) Non-conductors of electricity (graphite is an exception)	C (diamond) SiO_2 (quartz) C (graphite)

Solved Example 4-1

Identify the forces that must be overcome to cause melting in the following solids and rank the compounds in the increasing order of their expected melting points: **(a)** KF; **(b)** HF; **(c)** HCl; **(d)** F_2.

Solution

(a) Ion–ion; **(b)** hydrogen bonding and London forces; **(c)** dipole–dipole and London forces; **(d)** London forces only. The order of melting points: $F_2 < HCl < HF < KF$.

Solved Example 4-2

Identify the type of molecular solid in $H_2O(s)$, C(s), $CS_2(s)$, KF(s), Sn(s). Estimate the order of increasing melting points among them.

Solution

$H_2O(s)$ is a molecular solid. C(s) is a network solid. $CS_2(s)$ is a molecular solid. KF is an ionic solid. Sn is a metallic solid. The network and ionic solids should have the highest melting points, and the molecular solids should have the lowest value. $H_2O(s)$ has hydrogen bonding, a stronger force than the London forces in $CS_2(s)$. Therefore, the order of increasing melting points should be $CS_2 < H_2O < Sn < KF < C$.

Solved Example 4-3

Describe the differences between molecular solids and network covalent solids on atomic and macroscopic scales.

Solution

On the atomic scale, molecular solids are composed of individual molecules held together by intermolecular forces. Network covalent solids are composed of a three-dimensional array of atoms held together by covalent bonds. On the macroscopic scale, network covalent solids have high melting points and molecular solids have relatively low melting points.

4.2 | CRYSTAL LATTICES AND UNIT CELLS

A solid material in which the constituent atoms, molecules, or ions are arranged in an ordered pattern extending in all three spatial dimensions is known as **crystal** or **crystalline solid**. A crystal is a homogeneous portion of the solid substance that has a regular pattern of structural units bound by plane surfaces. It has long-range order and the constituent elements are arranged in a pattern that repeats periodically in the three directions. The characteristic features of a crystal are:

1. **Faces:** These are generally planar surfaces, arranged on a definite plane depending on internal geometry, by which the crystal is bound. Crystals may have like or unlike faces.
2. **Edges:** These are formed by the intersection of two adjacent faces of a crystal.
3. **Interfacial angle:** It is the angle between the normal to the two intersecting faces.
4. **Zone and zone axis:** The set of faces which meet in parallel edges or would do so if the planes of the faces are extended constitute a zone. The line passing through the centre of the crystal in a direction parallel to the edge of zone is called the zone axis.

Note: The relation between faces (F), edges (E) and interfacial angle (C) for a crystal is given by:

$$F + C = E + 2$$

A crystal is said to be symmetric if it has plane of symmetry, axis of symmetry and center of symmetry as shown in Fig. 4.5. These symmetry elements are discussed as follows.

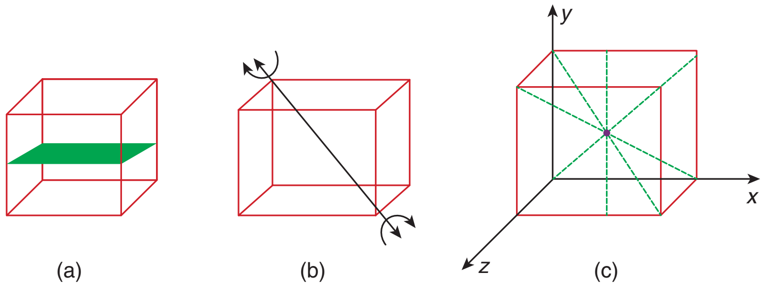


Figure 4.5 (a) Plane of symmetry. (b) Axis of symmetry. (c) Center of symmetry.

1. **Plane of symmetry:** A plane passing through the center of the crystal such that it divides the crystal into two equal portions that are mirror images of each other. These are of two types:
   - **(a)** Rectangular plane of symmetry: These are planes of symmetry which are located midway parallel to the opposite faces. Thus, in a cube (which has 6 faces) three rectangular planes of symmetry are possible as shown in Fig. 4.6.

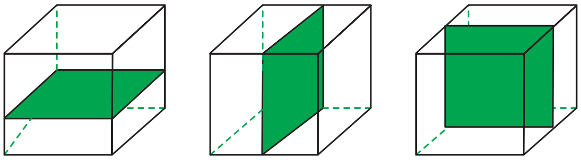


Figure 4.6 Rectangular planes of symmetry in a cube.

(b) Diagonal plane of symmetry: These are planes of symmetry that touch the opposite edges. They lie on the diagonal of opposite faces. Thus in a cube (which has 12 edges or 6 pairs of opposite edges), six diagonal planes of symmetry are possible (Fig. 4.7).

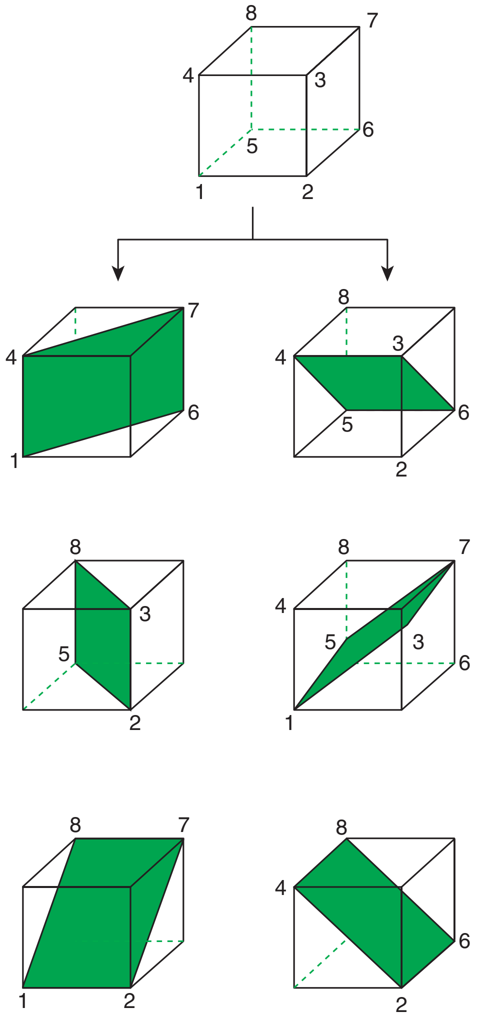


Figure 4.7 Diagonal planes of symmetry in a cube.

In Fig. 4.7, the diagonal planes of symmetry are:

(1, 4, 6, 7); (3, 4, 5, 6)
(2, 3, 5, 8); (1, 3, 5, 7)
(1, 2, 7, 8); (2, 4, 6, 8)

Therefore, total number of planes of symmetry in a cube = 3 (rectangular planes of symmetry) + 6 (diagonal plane of symmetry) = 9

2. **Axis of symmetry:** A line about which the rotation of the crystal results in the same appearance more than once in one complete revolution. These are of three types:

   (a) Axis of four-fold symmetry: If we make a line passing through the centers of two opposite faces of cube, on rotating the cube above this line as axis, the identical appearance of the cube occurs four times during its rotation by 360°. Simply put, we get identical appearance of the cube at every rotation of 90°. In a cube (which has six faces), there are three axis of four fold symmetry (Fig. 4.8).

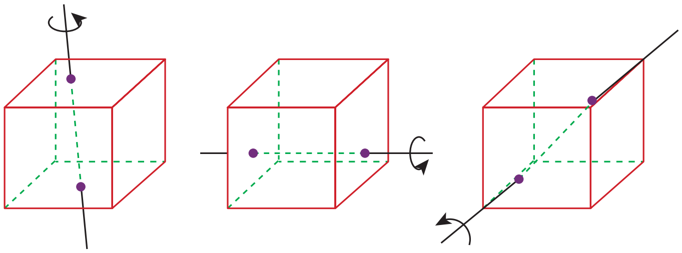


Figure 4.8 Axis of four-fold symmetry.

   (b) Axis of three-fold symmetry: If we make a line passing through opposite corners of a cube along the body diagonal, on rotating the cube above this line as axis, the identical appearance of the cube occurs three times during its rotation by 360°. In other words, we get identical appearance of the cube at every rotation of 120°. In a cube (which has eight corners or four pairs of diagonally opposite corners), there are four axis of three fold symmetry (Fig. 4.9).

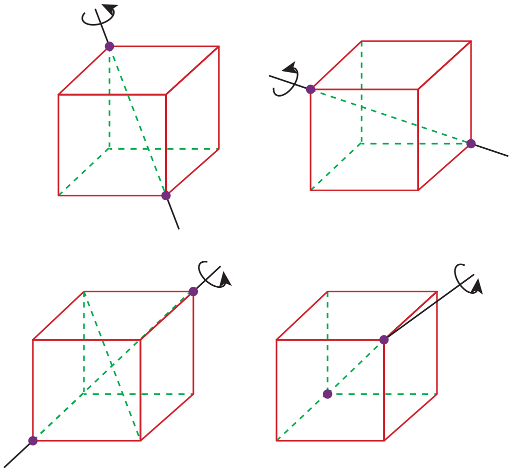


Figure 4.9 Axis of three-fold symmetry.

   (c) Axis of two-fold symmetry: If we have a line passing through the centers of two diagonally opposite edges of a cube, on rotating the cube above this line as axis, we get identical appearance of the cube two times during the rotation of cube by 360°. Thus, we get identical appearance at every 180° rotation of the cube. In a cube (which has 12 edges or six diagonally opposite pair of edges), six axis of two fold symmetry are possible (Fig. 4.10).

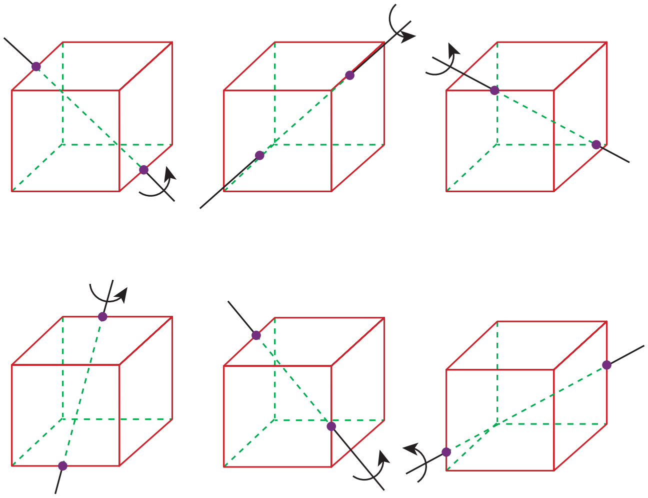


Figure 4.10 Axis of two-fold symmetry.

Therefore, the total number of axes of symmetry in a cube

$$= \underset{\text{(four fold)}}{3} + \underset{\text{(three fold)}}{4} + \underset{\text{(two fold)}}{6} = 13$$

3. **Center of symmetry:** The point in the crystal located such that any line passing through it divides the crystal into two symmetric portions. A crystal can never have more than one center of symmetry, which lies at the center of the cube. Therefore, total elements of symmetry in a cube = 9 + 13 +1 = 23.

A regular arrangement of the constituent particles of a crystal in a three-dimensional space is called **crystal lattice** or **space lattice**. The characteristics of a crystal lattice are:

1. Each point in a crystal lattice is known as lattice point or lattice site.
2. Each point in a crystal lattice represents a constituent particle which can be an atom, ion or a molecule.
3. Lattice points when joined by straight lines define the geometry of the lattice.

The unit cell is the smallest three-dimensional portion of a complete space lattice, which when repeated over and again in different directions produces the complete space lattice. The relation between unit cell and crystal lattice is that the unit cell is part of the lattice as shown in Fig. 4.11. The characteristics of a unit cell are:

1. The size of the unit cell is defined using **lattice parameters** (also called lattice constants or cell parameters).
2. These are the relative dimensions of the three edges a, b, c of the unit cell along the three axes (**primitives**) and the angles (**interfacial angles**) between these edges are given by α (angle between b and c); β (angle between a and c) and γ (angle between a and b).
3. The position of the atoms in the unit cell is defined by its coordinates (x_i, y_i, z_i) along the **crystallographic axes** (Fig. 4.11). These are lines drawn parallel to the lines of intersection of any three faces of the unit cell which do not lie in the same plane.

Crystal Systems

The types of unit cell are broadly categorized into primitive and non-primitive unit cells.

1. **Primitive unit cell:** In these unit cells, the constituent particles (atoms, ions or molecule) are present only at the corners of the unit cell. The shapes of unit cells are restricted by symmetry as well as space considerations, that is, they should be able to arrange themselves in the lattice without gaps and overlaps. Accordingly, there are seven unique and basic unit-cell shapes (primitive unit cells) with varying elements of symmetry in a three-dimensional space. These are called the **seven crystal systems**, namely, **cubic**, **tetragonal**, **orthorhombic**, **hexagonal**, **rhombohedral**, **monoclinic** and **triclinic** (Fig. 4.12). The lattice parameters and some examples of each kind are given in Table 4.3.

Table 4.3 Seven primitive unit cells and their parameters

Crystal system	Edge lengths	Angles	Examples
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	NaCl, ZnS, Cu
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	White Sn, SnO_2, TiO_2, $CaSO_4$
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	Rhombic sulphur, KNO_3, $BaSO_4$
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°; \gamma = 120°$	Graphite, ZnO, CdS
Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	Calcite ($CaCO_3$), HgS (cinnabar)
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90°; \beta \neq 90°$	Monoclinic sulphur, $Na_2SO_4 \cdot 10H_2O$
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	$K_2Cr_2O_7$, $CuSO_4 \cdot 5H_2O$, H_3BO_3

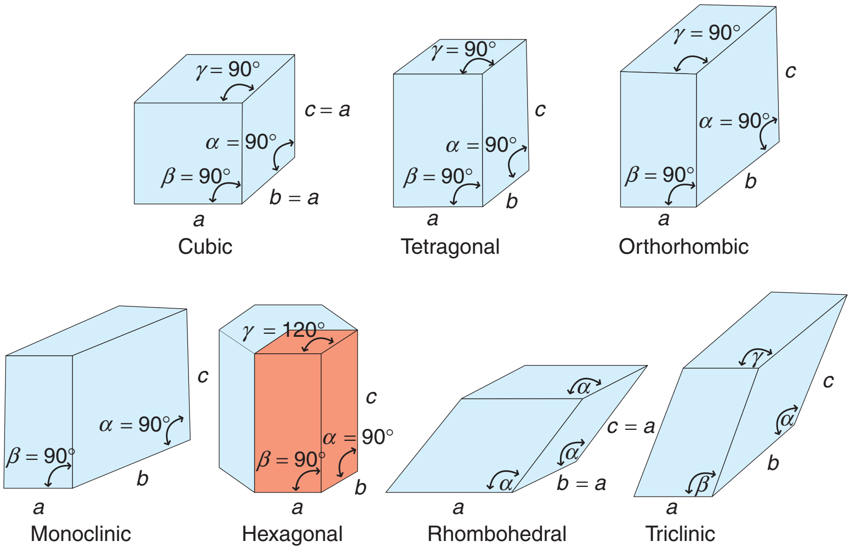
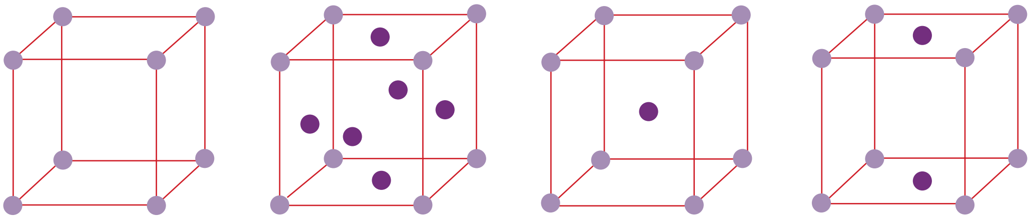


Figure 4.12 Types of primitive unit cells.

2. **Non-primitive unit cell:** In these unit cells, the constituent particles (atoms, ions or molecules) are present at the corners a well as on some other positions of the unit cell (say faces, edges, etc.) The non-primitive unit cells are further classified (Fig. 4.13) as follows:
   - **(a) Body centered:** Atoms are present at the corners and one at the center of the unit cell. The crystal systems with this type of unit cell include cubic, tetragonal and orthorhombic.
   - **(b) Face centered:** Atoms are present at the corners and at the center of each face of the unit cell. The crystal systems with this type of unit cell include cubic and orthorhombic.
   - **(c) End centered:** Atoms are present at the center of diagonal joining the nearest neighbors at one set of faces in addition to the atoms at the corner of the unit cell. The crystal systems with this type of unit cell are orthorhombic and monoclinic.



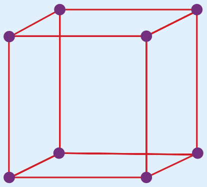
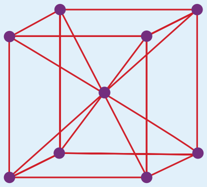
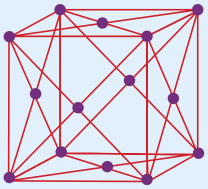
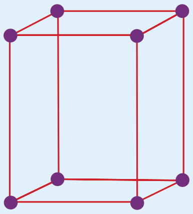
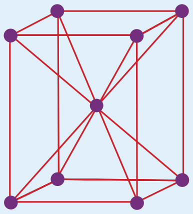
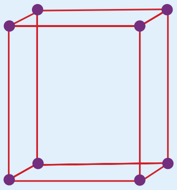
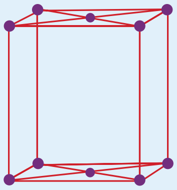
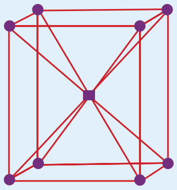
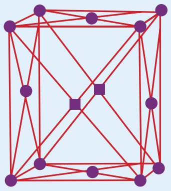
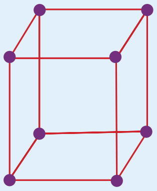
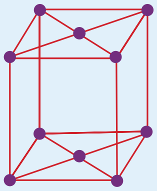
Primitive   Face centered   Body centered   End centered

Figure 4.13 Types of lattices in unit cells.

Bravais Lattices

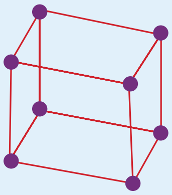
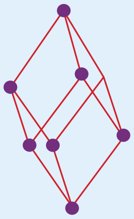
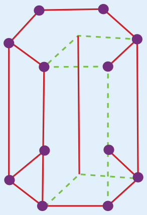
Although each crystal system is expected to have four different unit cells, all of them cannot exist in each case. Symmetry indicates that on combining 7 crystal classes with 4 possible unit cell types, only 14 three-dimensional lattice types (7 primitive or simple, 3 body centered, 2 face centered and 2 end centered) are possible. In 1848, Auguste Bravais demonstrated that, based on geometry, there are, in fact, only 14 possible ways in which similar lattice points can be arranged in regular order in three-dimensional space while maintaining their translational symmetry. For his efforts, crystal lattices are often referred to as **Bravais lattices**. Thus, there are 3 different cubic types, 2 different tetragonal types, 4 different orthorhombic types, 2 different monoclinic types, 1 rhombohedral type, 1 hexagonal type and 1 triclinic type which constitute the 14 Bravais lattices (Table 4.4).

Table 4.4 Crystal classes and Bravais lattices

Crystal classes	Bravais lattices
Cubic	 Primitive  Body centered  Face centered
Tetragonal	 Primitive  Body centered
Orthorhombic	 Primitive  End centered  Body centered  Face centered
Monoclinic	 Primitive  End centered

(Continued)

Table 4.4 (Continued)

Crystal classes	Bravais lattices
Triclinic	 Primitive
Rhombohedral or trigonal	 Primitive
Hexagonal	 Primitive

Solved Example 4-4

Name the Bravais lattices for the orthorhombic crystal class.

Solution

The Bravais lattices for the orthorhombic crystal class are primitive, end centered, body centered, face centered. The parameters are $a \neq b \neq c$ and $\alpha = \beta = \gamma = 90°$.

Solved Example 4-5

Which crystal systems have $\alpha = \beta = \gamma = 90°$?

Solution

Cubic, tetragonal and orthorhombic.

Solved Example 4-6

Which are the most unsymmetrical and symmetrical systems?

Solution

Most symmetrical is cubic as all the unit cell parameters are equal, that is, $a = b = c$ and $\alpha = \beta = \gamma = 90°$, for example, NaCl and KCl.

The most unsymmetrical is triclinic as all the parameters are unequal $a \neq b \neq c$ and $\alpha \neq \beta \neq \gamma \neq 90°$.

4.3 | CALCULATIONS INVOLVING UNIT CELL DIMENSIONS

A crystal lattice is composed of large number of unit cells in which the lattice points are occupied by constituent particles, which may be atoms, molecules or ions. However, it must be remembered that atoms located at the corners, edges and faces of the unit cell only partially occupy the unit cell, and are not fully contained in a single unit cell.

A primitive cubic lattice is of three types – simple cubic, body centered cubic and face centered cubic. The cubic lattice can be analyzed for the following:

1. **Number of atoms:** The number of atoms contained within the unit cell can be calculated by adding the contribution of each constituent particle to the unit cell.
   - **(a)** An atom at the corner of a unit cell is shared by eight unit cells. Hence each atom contributes 1/8 to the unit cell.
   - **(b)** An atom at the face is a shared by two unit cells, contributing 1/2 to the unit cell.
   - **(c)** An atom within the body of the unit cell is shared by no other unit cell. Hence, each atom contributes 1 to the unit cell.
   - **(d)** An atom present on the edge is shared by four unit cells. Hence, each atom on the edge contributes 1/4 to the unit cell.
2. **Effective number of atoms (z_{eff}):** The effective number of atoms in a unit cell can be determined as follows:

$$z_{\text{eff}} = \frac{n_c}{8} + \frac{n_f}{2} + \frac{n_b}{1} + \frac{n_e}{4}$$

where

n_c = number of atoms at corners of a unit cell

n_f = number of atoms at faces of a unit cell

n_b = number of atoms at body center of a unit cell

n_e = number of atoms at edges of a unit cell

Note: (a) Effective number of atoms at alternate faces of a unit cell: In a unit cell, there are only two alternate faces, therefore

$$z_{\text{eff}} = \underset{\substack{\text{Number of}\\\text{alternate}\\\text{faces}}}{2} \times \underset{\substack{\text{Contribution}\\\text{of face}\\\text{centered atom}}}{\left(\frac{1}{2}\right)} = 1 \text{ atom/unit cell}$$

(b) Effective number of atoms at alternate edge centers: In a unit cell, there are four alternate edge centers, therefore,

$$z_{\text{eff}} = \underset{\substack{\text{Number of}\\\text{edge centers}}}{4} \times \underset{\substack{\text{Contribution}\\\text{of atom at}\\\text{edge center}}}{\left(\frac{1}{4}\right)} = 1 \text{ atom/unit cell}$$

3. **Mass of the unit cell:** The mass of the atoms in a unit cell can be calculated as follows:

$$\text{Mass of the atoms of unit cell} = \text{Number of atoms in a unit cell} \times \text{Mass of an atom } (M_{\text{atom}})$$

$$\text{Mass of one atom} = \frac{\text{Atomic mass } (A)}{\text{Avogadro number } (N_A)}$$

4. **Volume of unit cell:** The volume of unit cell for a cubic unit cell is

$$V_c = a^3$$

5. **Density calculation:** It is possible to calculate the theoretical density of a compound. Since density is mass per unit volume, it can be calculated by finding the total atomic weight of all atoms in the unit cell and dividing it by the volume of the unit cell. Conversely, if we know the density of the substance and its crystal structure from experiment, then we can calculate the unit cell dimensions and hence the atomic mass of an element.

$$\text{Density } (\rho) = \frac{(\text{Number of atoms/cell}) \times (\text{Atomic mass})}{(\text{Volume of unit cell}) \times (\text{Avogadro's number})}$$

or

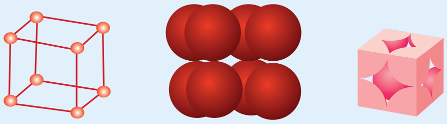
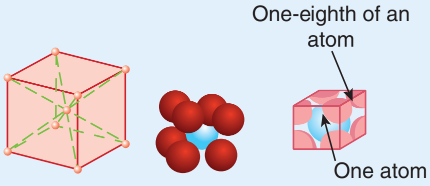
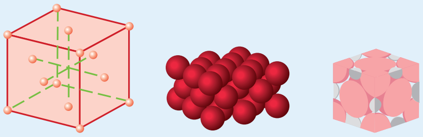
$$\rho = \frac{nA}{V_c \times N_A} \tag{4.1}$$

6. **Volume of space occupied:** The volume of occupied space contained within the unit cell is calculated by multiplying the number of atoms per unit cell by the volume of a sphere ($V = 4/3\pi r^3$).

4.4 | CUBIC LATTICE – SIMPLE, FACE CENTERED AND BODY CENTERED

Applying the above calculations, the various parameters of the three types of unit cell can be calculated as shown in Table 4.5.

Table 4.5 Various parameters of simple, face centered and body centered cubic lattice

Simple cubic	Body centered cubic (bcc)	Face centered cubic (fcc)
Edge length: In simple cubic packing, the atoms touch along the edge of the cube. Hence the cubic cell edge $a = 2r$, where R is the atomic radius.	Edge length: The hard spheres touch one another along cube diagonal. So, the cube edge length, $a = 4/\sqrt{3}$ (since diagonal of a cube = 3 times the length of one of its sides). The diagonal of the cube covers $R + 2R + R = 4R$ (as the middle sphere actually touches the two corner spheres).	Edge length: The hard spheres or ion cores touch one another across a face diagonal. Therefore, the cube edge length, $a = 2r\sqrt{2}$ [since $(4r)^2 = a^2 + a^2 \Rightarrow (a^2 = 8r^2)$].
		
Number of atoms per unit cell = (8 × 1/8) = 1 atom or rank $(z) = 1$	Eight atoms at the corners = 8 × 1/8 = 1 atom Atoms at the body center = 1 atom Number of atoms in a body centered cubic unit cell = 1 + 1 = 2 atoms or rank $(z) = 2$	One atom at each corner = (8 × 1/8 each) = 1 atom Atoms at each of the six face centers = (6 × 1/2 each) = 3 atoms Number of atoms in a face centered cubic unit cell = 4 atoms or rank $(z) = 4$
Number of nearest neighbors = 6	Number of nearest neighbors = 8	Number of nearest neighbors = 12
$\text{Mass} = \dfrac{\text{Atomic mass } (M_A)}{\text{Avogadro number } (N_A)}$	$\text{Mass} = 2 \times \dfrac{\text{Atomic mass } (M_A)}{\text{Avogadro number } (N_A)}$	$\text{Mass} = 4 \times \dfrac{\text{Atomic mass } (M_A)}{\text{Avogadro number } (N_A)}$
Volume, $V_c = a^3 = 8r^3$	Volume, $V = a^3 = \left(\dfrac{4r}{\sqrt{3}}\right)^3 = \left(\dfrac{64}{9}\right)\sqrt{3}r^3$	Volume, $V = a^3 = (2r\sqrt{2})^3 = 16r^3\sqrt{2}$

(Continued)

Table 4.5 (Continued)

Simple cubic	Body centered cubic (bcc)	Face centered cubic (fcc)
Density, $\rho = 1 \times \frac{M_A}{(2r)^3 N_A} = \frac{M_A}{8N_A r^3}$	Density, $\rho = \frac{2M_A/N_A}{(64/9)\sqrt{3}r^3} = \frac{9M_A}{32\sqrt{3}N_A r^3}$	Density, $\rho = \frac{4M_A/N_A}{16r^3\sqrt{2}} = \frac{M_A\sqrt{2}}{8N_A r^3}$
Volume of space occupied:	Volume of space occupied:	Volume of space occupied:
$V = \frac{4}{3}\pi r^3$	$V = 2 \times \frac{4}{3}\pi r^3 = \frac{8}{3}\pi r^3$	$V = 4 \times \frac{4}{3}\pi r^3 = \frac{16}{3}\pi r^3$

Some other important parameters related to cubic lattice can be determined as follows.

1. **Simple cubic:** In simple cubic cell (scc), coordination number is six and $a = 2r$. From Fig. 4.14, the distance of the nearest and second nearest atom in a simple cubic cell can be determined as follows.

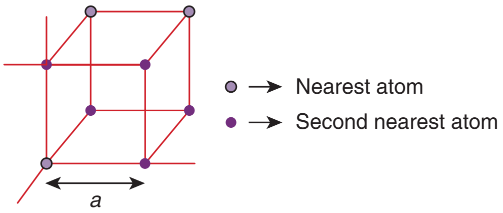


Figure 4.14 Simple cubic cell.

(i) Distance of the nearest atom from a given atom in scc.

$d = a = 2r$

Number of nearest atoms = 6.

(ii) Distance of the second nearest atom from a given atom in scc.

$$d = \sqrt{2}a = 2\sqrt{2}r$$

Number of second nearest atoms = 12

2. **Body centered cubic:** In a body centered cubic cell (bcc), the coordination number is 8 and $\sqrt{3}a = 4r$, as shown in Fig. 4.15. Then the distance of the nearest, second nearest and third nearest atom from a given atom can be determined as follows.

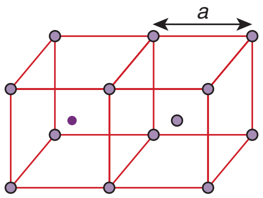


Figure 4.15 Body centered cubic cell.

(i) Distance nearest atom in bcc from a given atom

$$d = \frac{\sqrt{3}a}{2} = 2r$$

Number of nearest atoms = 8.

(ii) Distance of second nearest atom in bcc

$$d = a = \frac{4r}{\sqrt{3}}$$

Number of second nearest atoms = 6.

(iii) Distance of the third nearest atom $d = a\sqrt{2}$

(iv) Distance of fourth nearest atom in bcc can be determined as shown in Fig. 4.16.

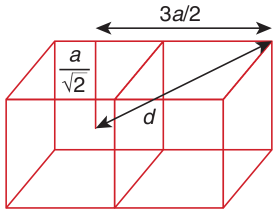


Figure 4.16 Distance of fourth nearest atom in bcc.

$$d = \sqrt{\left(\frac{3a}{2}\right)^2 + \left(\frac{a}{\sqrt{2}}\right)^2} = \frac{a\sqrt{11}}{2}$$

Number of fourth nearest neighbors = 24.

3. Face centered cubic: In a face centered cubic cell (fcc), the coordination number is 12 and $\sqrt{2}a = 4r$ as shown in Fig. 4.17. Then distance of the nearest atom and second, third and fourth nearest atoms can be determined as follows.

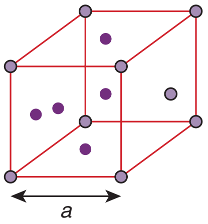


Figure 4.17 Face centered cubic cell.

(i) Distance of nearest atom from a given atom in fcc

$$d = \frac{a}{\sqrt{2}}$$

Number of nearest atoms = 12.

The layers in cubic close packing, ccp (ABCABC….) can be visualized as shown in Fig. 4.18.

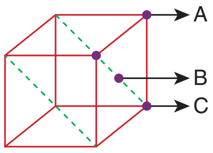


Figure 4.18 Visualizing layers in ccp.

(ii) Distance of second nearest atoms from a given atom in fcc $d = a$

Number of second nearest atoms = 6.

(iii) Distance of third nearest atoms from a given atom in fcc

$$d = \sqrt{a^2 + \left(\frac{a}{\sqrt{2}}\right)^2} = \sqrt{\frac{3}{2}}\,a$$

Number of third nearest atoms = 24.

(iv) Distance of fourth nearest atoms from an atom in fcc

$$d = a\sqrt{2}$$

Number of fourth nearest atoms = 12.

Solved Example 4-7

Iron metal and caesium chloride have similar structures. The simplest repeating unit in iron is a cube of eight iron atoms with a ninth iron atom in the center of the body of the cube. The simplest repeating unit in CsCl is a cube of Cl^- ions with a Cs^+ ion in the center of the body. Explain why one of the structures is classified as a body centered cubic unit cell and the other as a primitive cubic unit cell.

Solution

In order for a substance to be classified as a body centered cubic cell, all of the positions in the unit cell must be occupied by the same type of atom or ion.

Solved Example 4-8

For the three cubic structures studied, which has the simplest relationship between the radii of the ions and the edge length of the unit cell?

Solution

The simple cubic cell has the simplest relationship between the radii of the ions and the length of the edge of the unit cell. In a simple cubic cell, the length of the edge of the cell is equal to $r^+ + r^-$. In a face centered cube $2(r^+ + r^-) = a\sqrt{2}$ where a is the length of the edge of the unit cell. For a body centered cubic cell, the relationship is $2(r^+ + r^-) = a\sqrt{3}$.

Solved Example 4-9

Silver has a cubic unit cell with a cell edge of 480 pm. Its density is 10.6 g cm^{-3}. How many atoms of silver are there in the unit cell?

Solution

The length of the edge of unit cell = 408 pm, volume of unit cell = $(408 \text{ pm})^3 = 67.92 \times 10^{-24}\ cm^3 = a^3$. Thus,

Mass of unit cell = Density × Volume = $10.6 \text{ g cm}^{-3} \times 67.92 \times 10^{-24}\ cm^3 = 7.20 \times 10^{-24}$g

But mass of unit cell = number of atoms in unit cell × mass of each atom and mass of each atom is

$$\frac{\text{Atomic mass}}{N_A} = \frac{108}{6.023 \times 10^{23}} = 1.79 \times 10^{-22}\ \text{g}$$

Hence, the number of atoms present in a unit cell is

$$z = \frac{7.20 \times 10^{-22}}{1.79 \times 10^{-22}} = 4.02 \approx 4$$

Solved Example 4-10

Sodium metal crystallizes in body centered cubic lattice with the cell edge, a = 4.29 Å. What is the radius of sodium atom? **(IIT-JEE 1994)**

Solution

In a bcc arrangement, we have

$$r = \frac{\sqrt{3}a}{4} = \frac{\sqrt{3} \times 4.29}{4} = 1.86\ \text{Å}$$

Solved Example 4-11

A metal crystallizes into two cubic phases, face centered cubic (fcc) and body centered cubic (bcc), whose unit cell lengths are 3.5 Å and 3.0 Å, respectively. Calculate the ratio of densities of fcc and bcc. **(IIT-JEE 1999)**

Solution

The ratio of the densities of fcc to bcc is

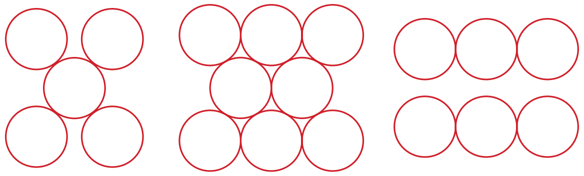
$$\frac{\rho_{\text{fcc}}}{\rho_{\text{bcc}}} = \frac{\dfrac{z_{\text{fcc}} \times M}{a_{fcc}^3 \times \text{Number of atoms}}}{\dfrac{z_{\text{bcc}} \times M}{a_{\text{bcc}}^3 \times \text{Number of atoms}}}$$

$$\text{or ratio} = \frac{z_{\text{fcc}}}{z_{\text{bcc}}}\left(\frac{a_{\text{bcc}}}{a_{\text{fcc}}}\right)^3 = \frac{4}{2} \times \left(\frac{3.0}{3.5}\right)^3$$

$$= \frac{432}{343} = 1.26$$

Solved Example 4-12

Fig. 4.19 shows the location of atoms in three crystallography planes in an fcc lattice. Draw the unit cell for the corresponding structure and identify these planes in your diagram.



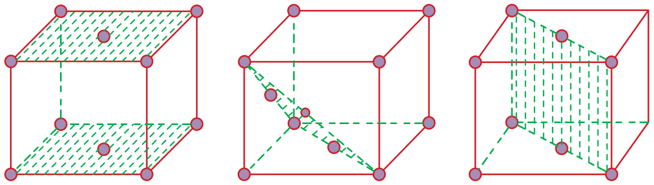
(a) (b) (c)

Figure 4.19

(IIT-JEE 2000)

Solution

The unit cells are shown in Fig. 4.20, and the shaded portions represent the planes.



(a) (b) (c)

Figure 4.20

Solved Example 4-13

The edge length of unit cell of a metal having molecular weight 75 g mol^{-1} is 5 Å which crystallizes in cubic lattice. If the density is 2 g cm^{-3} then find the radius of metal atom. ($N_A = 6.023 \times 10^{23}$). Give the answer in pm. **(IIT-JEE 2006)**

Solution

The density is given by $\rho = \dfrac{z \times M_A}{a^3 \times N_A}$

Therefore,

$$z = \rho \times a^3 \times \frac{N_A}{M_A}$$

$$= 2\text{ g cm}^{-3} \times (5 \times 10^{-8}\text{ cm})^3 \times \frac{(6.023 \times 10^{23}\text{ mol}^{-1})}{75\text{ g mol}^{-1}}$$

$$= 2$$

Thus, the metal has a bcc structure for which

$$r = \frac{\sqrt{3}a}{4} = \frac{1.732 \times 5}{4} = 2.165\text{ Å} = 216.5\text{ pm}$$

Solved Example 4-14

Gold (atomic radius = 0.144 nm) crystallizes in a face centered unit cell. What is the length of a side of the cell?

Solution

For an fcc structure, face diagonal $d = 4r$. If a is the edge length of the unit cell, face diagonal is equal to $\sqrt{2}a$. So, $\sqrt{2}a = 4r$. Therefore, the length of a side of the cell is

$$a = \frac{4}{\sqrt{2}} \times 0.144 = 0.407\text{ nm}$$

Solved Example 4-15

The edge length of the cubic unit cell of lead is 4.92 Å. The density of lead is 11.55 g cm^{-3}. What is the type of cubic lattice taken up by lead? (Atomic mass of lead = 207.2 u.)

Solution

Molar volume of the solid $= \dfrac{a^3}{n} \times 6.023 \times 10^{23}$ where a is the side length and n is the number of atoms in the unit cell. Also

$$\text{Molar volume} = \frac{\text{molar mass}}{\text{density}} = \frac{207.2}{11.55}$$

$$= \frac{(4.92\times 10^{-8})^3 \times 6.023\times 10^{23}}{n}$$

Substituting in the previous expression, we get

$$\frac{71.731}{n} = 17.939 \Rightarrow n = 4$$

Thus, lead has fcc arrangement.

Solved Example 4-16

A compound is formed by atom of elements A and B, which has a cubic structure. Atoms of element A are present at corner of the cube and also at the face centers. Atoms of B are present at the body center and at the edge center. Calculate z_{eff}, total number of atoms in the cube and simplest formula of the compound if

(a) All the atoms are removed from one of the body diagonals of the cube.

(b) All the atoms from the diagonals of one of the face of the cube are removed.

(c) All the atoms are removed from one of the plane passing through the middle of the cube.

(d) All the atoms are removed from one of the axis passing through one of the face centers of the cube.

Solution

Consider that the given compound has cubic structure as shown in Fig. 4.21.

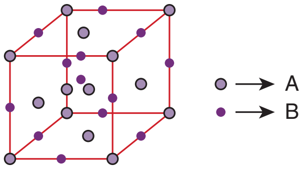


Figure 4.21

(a) Atoms are removed from one of the body diagonal, that is, 2 A atoms (from corner) + 1 B atom (from body center) are removed.

Therefore,

$$z_{\text{eff}} = \underset{\text{(no. of atoms of A at corners)}}{\frac{(8-2)}{8}} + \underset{\text{(no. of atoms of A at face center)}}{\frac{6}{2}} + \underset{\text{(no. of atoms B at body center)}}{\frac{(1-1)}{1}} + \underset{\text{(no. of atoms of B at edge center)}}{\frac{12}{4}} = \frac{27}{4}$$

Total number of atoms = 6 + 6 + 12 = 24 atoms
Simplest formula = $A_{15/4}B_3$ or $A_{15}B_{12}$

(b) Atoms are removed from two diagonals of one face of cube, that is, 4 A atoms (from corner) and 1 A atom (from face center) are removed. Therefore,

$$z_{\text{eff}} = \underset{\text{(no. of atoms of A at corners)}}{\frac{(8-4)}{8}} + \underset{\text{(no. of atoms of A at face center)}}{\frac{(6-1)}{2}} + \underset{\text{(no. of atoms B at body center)}}{\frac{1}{1}} + \underset{\text{(no. of atoms of B at edge center)}}{\frac{12}{4}} = 7$$

Total number of atoms = 4 + 5 + 1 + 12 = 22 atoms
Simplest formula = A_3B_4

(c) If all the atoms are removed along the plane passing through the middle of the cube, that is, 4 A atoms (from face centers), 4 B atoms (from edge centers), 1 B atom (from body center) are removed. Therefore,

$$z_{\text{eff}} = \underset{\text{(no. of atoms of A at corners)}}{\frac{8}{8}} + \underset{\text{(no. of atoms of A at face center)}}{\frac{(6-4)}{2}} + \underset{\text{(no. of atoms B at body center)}}{\frac{(1-1)}{1}} + \underset{\text{(no. of atoms of B at edge center)}}{\frac{(12-4\uparrow}{4}} = 4$$

Total number of atoms = 8 + 2 + 0 + 8 = 18 atoms
Formula = A_2B_2 or AB

(d) If all atoms are removed along an axis passing through one of the face center, that is, 1 B atom (from body center) + 2 A atoms (from face center) are removed. Therefore,

$$z_{\text{eff}} = \underset{\text{(no. of atoms of A at corners)}}{\frac{8}{8}} + \underset{\text{(no. of atoms of A at face center)}}{\frac{(6-2)}{2}} + \underset{\text{(no. of atoms B at body center)}}{\frac{(1-1)}{1}} + \underset{\text{(no. of atoms of B at edge center)}}{\frac{12}{4}} = 6$$

Total number of atoms = 8 + 4 + 0 + 12 = 24 atoms
Simplest formula = A_3B_3 or AB

4.5 | CLOSE-PACKING IN CRYSTALS

The crystal structures of many metals, alloys and inorganic compounds can be described geometrically as a packing of equal spheres (atoms), held together by interatomic forces. When the crystal is made up of more than one kind of atom, the positions of one kind of atoms or ions correspond to those of closely packed equal spheres and the other kind of atoms are distributed among the voids in the close-packing. Such structures are generally referred to as **close-packed structures**.

In order to maximize the bonding in such close-packed crystalline solids, the arrangement or packing of atoms needs to be such that maximum available space is utilized; hence, the crystal has maximum density. *In analyzing the efficiency of packing of atoms to meet these criteria, it is assumed that the atoms are hard spheres of identical size*. The three-dimensional structure for the constitutional particles can be built by understanding the packing in one, two and three dimensions.

Close Packing in One Dimension

In this case, the closest efficient packing is when the spheres just touch each other is shown in Fig. 4.22. The number of closest neighbors that an atom has is called its coordination number. In one-dimension packing, coordination number is two.

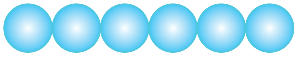


Figure 4.22 Close packing of sphere in one dimension.

Close Packing in Two Dimensions

The arrangement of spheres can be done by stacking the rows of closely packed spheres in two possible ways:

1. **Square close packing:** It is obtained when the second row of spheres is placed adjacent to the first row. The spheres in the two rows are thus aligned horizontally as well as vertically, as shown in the Fig. 4.23(a). If the first row is designated as “A”, then the second row being identical is also called “A”. When many such rows are stacked together, the arrangement is AAA type.

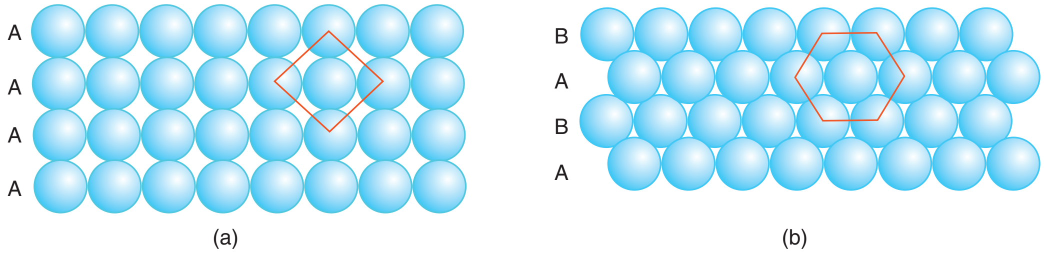


Figure 4.23 (a) Square and (b) hexagonal close packing of spheres.

In such an arrangement, each sphere or atom has four other atoms as its closest neighbors, so the coordination number is four. The centers of the neighboring spheres join to form a square and hence the packing is known as **square close packing in two dimensions**.

2. **Hexagonal close packing:** It is obtained when the second row of spheres is placed in the interstices or depressions of the first-row spheres as shown in Fig. 4.23(b). In this arrangement if the first row is called “A” type then the second row being different can be designated as “B” type. Then when the third row is placed in a staggered manner over the second row, it is aligned with first row and can be “A” type. Similarly, the fourth row would be staggered with respect to third row but aligned with second row and is hence “B” type. The arrangement is known as ABAB type. This packing is more efficient with less free space and is a more efficient way of packing in two-dimensional space.

   In this arrangement, each sphere or atom has six closest neighbors, so coordination number is six. The centers of the neighboring squares form a hexagon and hence the packing is known as **hexagonal close packing (hcp) in two dimensions**. It can be seen from Fig. 4.23(b) that there are some empty spaces or voids between the spheres placed in ABAB type of packing. These voids are triangular in shape and are known as triangular voids. These are of two types—one with the apex of the triangle pointing upwards and in the other pointing downwards.

Close Packing in Three Dimensions

The arrangement or packing of constituent atoms in three-dimensional space can be derived by further extending the packing to three-dimensional space on a square or hexagonal close packed two-dimensional stack. This can be generated by stacking two-dimensional layers one above the other.

From Two-Dimensional Square Close Packing

In this arrangement, the second layer of atoms is placed above the first layer, similar to how it is placed adjacent in square close packing in two dimensions. The arrangement of spheres is perfectly aligned horizontally as well as vertically. The subsequent layers may be placed one above the other in a similar manner to build a lattice that has "AAA…" type of pattern. The lattice so generated is the simple cubic lattice where the primitive cubic cell is the unit cell.

From Two-Dimensional Hexagonal Close Packing

Three-dimensional close packed structure can be obtained from the two-dimensional arrangement of hexagonal close packing by placing layers one over the other.

1. **Placing second layer over the first layer:** In this arrangement, the second layer of spheres is placed in the depression created by the first layer "A" as shown in Figs. 4.24(a) and (b). Since the spheres of the two layers are aligned differently, the second sphere may be labeled as "B". It is to be noted that although there are six voids around each sphere in the first layer, only three of these can be directly covered by placing the spheres of the second layer.

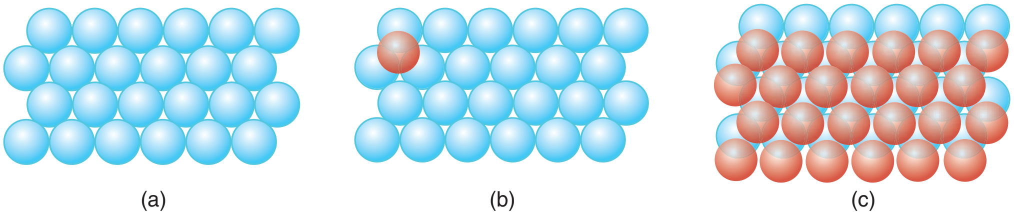


Figure 4.24 (a) One layer of closely packed spheres. (b) A second layer is started by placing a sphere (colored red) in a depression formed between three spheres in the first layer. (c) A second layer of spheres shown slightly transparent so we can see how the atoms are stacked over the first layer.

2. **Placing third layer over the second layer:** Placing the second layer of spheres in any of the two types of voids is identical. The difference between the two close-packed structures lies in the relative orientations of the spheres in the first layer and those that form the third layer. When it comes to placing the spheres of the third layer, we again have two different possibilities arising:
   - **(a)** The spheres of the third layer can be placed in the voids of the spheres of second layer such that they are exactly in the same positions as the spheres of first layer as shown in Fig. 4.25(a). If the spheres of the first layer are labeled as A, those of second layer as B, then the third layer is also labeled A. Hence, the pattern in this type of packing is ABABAB… and is called hexagonal close packing or hcp. Each atom in an hcp lattice is surrounded by and touches 12 nearest neighbors, 6 are in the planar hexagonal array (B layer), and 6 (3 in the A layer above and 3 in the A layer below) form a trigonal prism around the central atom. Examples of hcp are Mg, Zn, Cd.

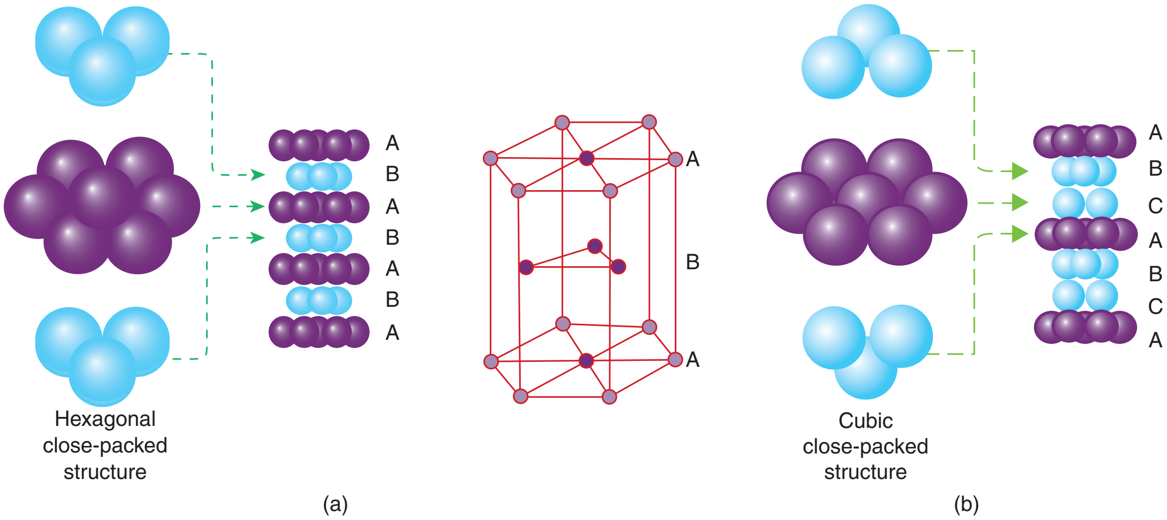

A
B
A
B
A
B
A
A
B
A
Hexagonal close-packed structure
(a)
A
B
C
A
B
C
A
Cubic close-packed structure
(b)

Figure 4.25 (a) Hexagonal close-packed structure with ABABAB… repeating pattern. (b) Cubic close-packed structure with ABCABCABC… repeating pattern.

(b) Alternately, if the atoms in the third layer are placed such that they are on the positions corresponding to the three voids in the A layer that were *not* covered by the atoms in the B layer, then the third layer is different from either A or B and is labeled C. If a fourth layer is placed then it repeats the A layer orientation, and succeeding layers repeat the pattern ABCABCA…, the resulting closest packed structure is called as cubic close packing [ccp; Fig. 4.25(b)]. Examples of ccp are Cu and Ag.

The similarities and differences between hexagonal and cubic close-packed structures can be understood by comparing Figs. 4.25(a) and (b).

1. In the hexagonal close-packed structure, the atoms in the first and third planes lie directly above each other. In the cubic close-packed structure, the atoms in those planes are oriented in different directions.
2. In both hexagonal and cubic closed packing, an atom/sphere is in contact with 6 others in its own layer; it directly touches 3 spheres in the layer above and 3 in the layer below. Thus, each sphere has 12 closest neighbors. Thus, in both hcp and ccp each sphere has a coordination number of 12 and this is the maximum coordination number of any sphere for a maximum packing density.
3. Because of their shape, spheres cannot fill space completely. In a close-packed arrangement of spheres, 74% of the space is filled. Thus, 26% of the space is unoccupied, and may be regarded as holes in the crystal lattice. These vacant spaces are known as **interstitial voids** or **interstices**. Many common crystal structures are related to, and may be described in terms of, hexagonal or cubic close-packed arrangements.

Body Centered Cubic Close Packing

There is a third method of packing the spheres in three-dimensions and is known as body centered cubic close packing (bccp). In this arrangement, the spheres in the first layer are slightly opened up in a manner that none of them touch each other. The spheres in the second layer are placed at the top of the hollow spaces in the first layer and the spheres in the third layer are placed exactly as in the first layer (Fig. 4.26). So, each sphere in this packing arrangement is in contact with eight other spheres, that is, four in the layer above and four in the layer below. Hence, the coordination number is eight.

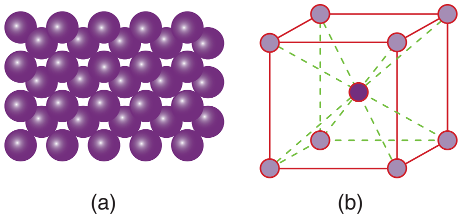


Figure 4.26 (a) Body centered close packing of spheres. (b) Body centered close packing.

Coordination Number in Hexagonal Close Packing (hcp) and Cubic Close Packing (ccp)

Coordination numbers is the number of nearest neighbors of any atom in a lattice.

For hcp structure, the number of nearest neighbors of an atom is 12 as can be seen from Fig. 4.27. Thus, the coordination number is 12. Example of elements in hcp lattice type are Mg, Cd, Zn, Ti and Be.

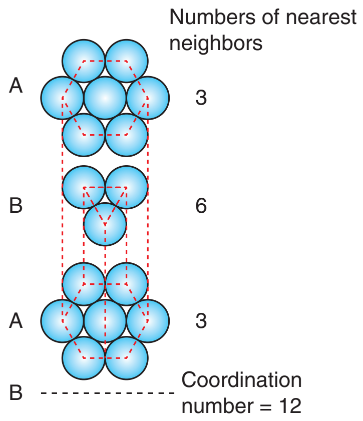


Figure 4.27 Coordination number in hcp.

For cubic close packing structure, the number of nearest neighbors of an atom is 12 (Fig. 4.28), hence the coordination number is 12.

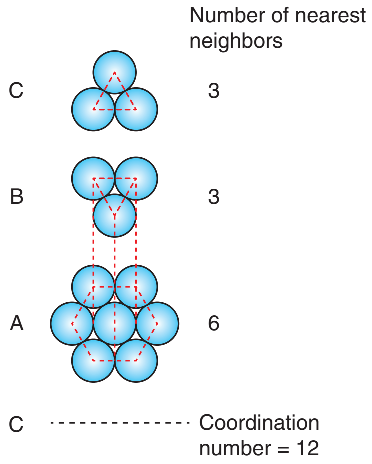


Figure 4.28 Coordination number in ccp.

Examples of elements in ccp lattice type are Ca, Sr, Ag, Au and Cu.
Examples of elements in bcc lattice type are Li, Na, K, Rb and Cs.

4.6 | PACKING EFFICIENCY AND PACKING FRACTION

The packing efficiency, *f*, is defined as the fraction of the total volume of the unit cell actually occupied by atoms.

$$\text{Packing efficiency} = \frac{\text{Volume occupied by atoms/spheres}}{\text{Total volume of the unit cell}} \times 100 \qquad (4.2)$$

1. **For a simple cubic (sc) structure:** For such an arrangement, the unit cell edge is $a = 2R$, since two spheres just touch each other along the edge. Here R is the radius of the sphere. There is one atom per unit cell of a simple cubic structure. Therefore,

$$\text{Packing efficiency} = \frac{1 \times (4/3)\pi R^3}{(2R)^3} \times 100 = \frac{\pi}{6} \times 100 = 52.35\%$$

2. **For body centered cubic (bcc) structure:** Similarly for a bcc structure, the spheres touch each other along the body diagonal. Hence unit cell edge a is

$$a = \frac{4R}{\sqrt{3}} \quad \text{or} \quad R = \frac{\sqrt{3}a}{4}$$

In bcc structure, the total number of atoms per unit cell is 2. Volume of two spheres is

$$2 \times \frac{4}{3}\pi R^3$$

Volume of the cube is

$$a^3 = \left(\frac{4}{\sqrt{3}}R\right)^3$$

Therefore,

$$\text{Packing efficiency} = \frac{2\times(4/3)\pi R^3}{(4/\sqrt{3}R)^3}\times 100 = \frac{(8/3)\pi R^3\times 100}{64/3\sqrt{3}R^3} = 68\%$$

and packing fraction is 0.68.

3. **In cubic close packing or face centered cubic (fcc) arrangement:** For such an arrangement, along each face one sphere touches two others along the diagonal.

In ccp unit cell, eight spheres are present at the corners of the unit cell and six are present at each of the faces. The structure is similar to face centered cubic unit cell. Therefore, the number of atoms per unit cell is four. Let the radius of spheres in cubic close packing be r and the edge length of the unit cell be a (Fig. 4.29). Then in the right angled triangle ABC,

$$\mathrm{AC}^2 = \mathrm{AB}^2 + \mathrm{BC}^2 = a^2 + a^2 = 2a^2$$

Therefore, $\mathrm{AC} = \sqrt{2}a$

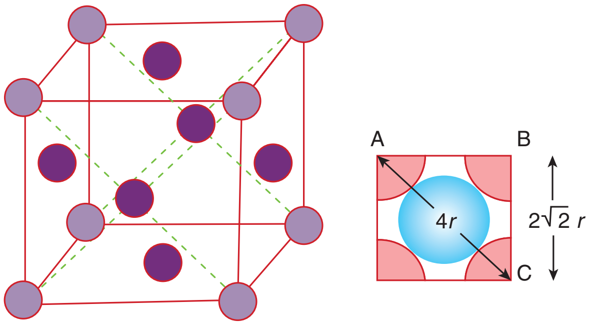


Figure 4.29 Packing efficiency in ccp.

We can see from Fig. 4.29 that AC is also the face diagonal, so in terms of radius of the spheres, AC = $4r$. Therefore,

$$\sqrt{2}a = 4r \quad \text{or} \quad a = \frac{4r}{\sqrt{2}} = 2\sqrt{2}r$$

The volume of the unit cell is $a^3 = (2\sqrt{2}r)^3 = 16\sqrt{2}r^3$.

Volume of the four spheres $= 4\times\frac{4}{3}\pi r^3 = \frac{16}{3}\pi r^3$

The unit cell is occupied by four spheres (atoms). Hence, the volume of unit cell occupied is

$$\text{Packing efficiency} = \frac{\text{Volume of four spheres in the unit cell}}{\text{Total volume of the unit cell}}\times 100$$

$$= \frac{16/3\pi r^3}{16\sqrt{2}r^3}\times 100 = \frac{\pi}{3\times\sqrt{2}}\times 100 = 74\%$$

Therefore the volume of unit cell occupied is 74% and packing fraction is 0.74.

4. **In hexagonal close packing:** In the hcp unit cell (Fig. 4.30, there are 12 spheres (atoms) at the corners, which are shared by six other unit cells; one sphere at the center of top and bottom faces, each shared by two units; and three spheres at the center of the body. Thus, the number of spheres (atoms) in a hcp unit cell are:

$$12\times\frac{1}{6}(\text{corners}) + 2\times\frac{1}{2}(\text{face centers}) + 3(\text{in body}) = 6$$

Volume of the unit cell = Base area × height

Base area of a regular hexagon $= 6\times\frac{\sqrt{3}}{4}(2r)^2 = 6\times\sqrt{3}\,r^2$

Height of the unit cell $(h) = 4r\times\sqrt{\frac{2}{3}}$

Therefore,

Volume of the unit cell $= 6\times\sqrt{3}\,r^2\times 4r\times\sqrt{\frac{2}{3}} = 24\sqrt{2}r^3$

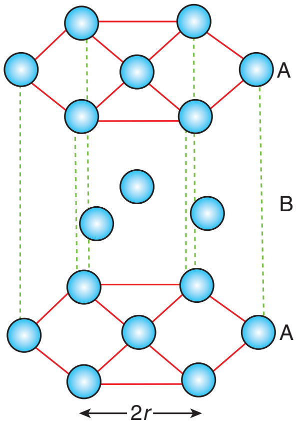


Figure 4.30 Packing efficiency in hcp.

Volume of unit cell occupied by six spheres $= 6\times\frac{4}{3}\pi r^3 = 8\pi r^3$

$$\text{Packing efficiency} = \frac{\text{Volume of six spheres in the unit cell}}{\text{Total volume of the unit cell}}\times 100$$

$$= \frac{8\pi r^3}{24\sqrt{2}r^3}\times 100 = \frac{\pi}{3\times\sqrt{2}}\times 100 = 74\%$$

and packing fraction is 0.74.

Calculation of Height of Unit Cell in Hexagonal Close Packing

Consider the base layer of hcp structure as shown in Fig. 4.31(a).

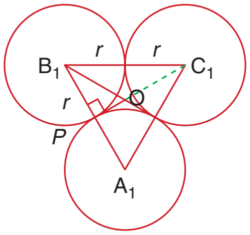


Figure 4.31(a) Base layer of hcp structure.

In triangle A_1PC_1

$$(PC_1)^2 + r^2 = (2r)^2$$
$$PC_1 = \sqrt{3}r$$

Since the medians intersect each other in the ratio 2:1, therefore,

$$OP = \frac{2}{3}(PC_1) = \frac{2}{3}\sqrt{3}r = \frac{2r}{\sqrt{3}}$$

Let the total distance between the layer ABA… $= C$

Therefore, distance between layer AB $= \frac{C}{2}$.

Point O is the intersection of medians, therefore, from Fig. 4.31(b)

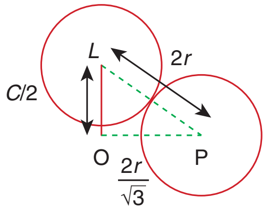


Figure 4.31(b) Calculation of height in hcp structure.

$$\left(\frac{C}{2}\right)^2 + \left(\frac{2r}{\sqrt{3}}\right)^2 = 2r^2$$

$$C = 4r\sqrt{\frac{2}{3}}$$

Solved Example 4-17

A metallic clement crystallizes into a lattice containing a sequence of layers ABABAB…. Any packing of spheres leaves out voids in the lattice. What percentage by volume of this lattice is empty space? **(IIT-JEE 2006)**

Solution

The sequence ABABAB… indicates hcp unit cell. Now, there are 6 atoms per unit cell and volume of the unit cell is $24\sqrt{2}\,r^3$. Thus, the packing fraction is

$$\text{Packing efficiency} = \frac{\text{Volume of 6 spheres in the unit cell}}{\text{Total volume of the unit cell}} \times 100$$

$$= \frac{6 \times \frac{4}{3}\pi r^3}{24\sqrt{2}r^3} \times 100$$

$$= \frac{\pi}{3 \times \sqrt{2}} \times 100 = 74\%$$

Hence, the percentage of empty space = 100 – 74 = 26%

Solved Example 4-18

Calculate the efficiency (percentage of volume occupied and unoccupied) of packing in case of a metal crystal for primitive cubic.

Solution

Consider the figure of primitive cubic unit cell as shown in Fig. 4.32:

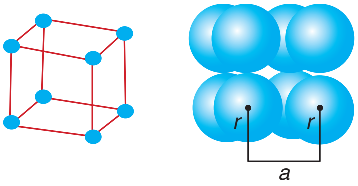


Figure 4.32

From the figure, we have $a = 2r$ where a is the edge length and r is the radius of the sphere. Then, number of spheres present per unit cell = 8 × 1/8 = 1

$$\text{Volume of sphere} = 4/3\pi r^3$$

$$\text{Volume of cube} = a^3 = (2r)^3 = 8r^3$$

$$\text{Packing efficiency} = \frac{4/3\pi r^3}{8r^3} = 52.4\%$$

So, the percentage of unoccupied volume = 100 – 52.4 = 47.6%

Solved Example 4-19

The density of solid argon is 1.65 g mL^{-1} at –233°C. If the argon atom is assumed to be sphere of radius 1.54×10^{-8} cm, what percentage of solid argon is empty space? (Atomic weight of Ar = 40 u.)

Solution

Given that density = 1.65 g cm^{-3}, so the number of atoms in 1 cm^3 $= \frac{1.65}{40} \times 6.023 \times 10^{23} = 2.48 \times 10^{22}$

Now, volume of one atom of Ar $= \frac{4}{3}\pi r^3$. So, the total volume of all Ar atoms is

$$\text{Total volume} = \frac{4}{3}\pi r^3 \times 2.48 \times 10^{22}$$

$$= \frac{4 \times 3.14 \times (1.54 \times 10^{-8})^3 \times 2.48 \times 10^{22}}{3}$$

$$= 0.38 \text{ cm}^3$$

Therefore, % of space occupied by solid argon is

$$\frac{\text{Total volume}}{\text{Volume of solid argon}} = \frac{0.38}{1} \times 100 = 38\%$$

The percentage of empty space = 100 – 38 = 62%.

Solved Example 4-20

The unit cell of metallic silver is face centered cubic (or cubic closed-packed) with $a = b = c = 4.086$ Å. Calculate **(a)** the radius of Ag atom, **(b)** the volume of an Ag atom, **(c)** volume of a unit cell that is occupied by Ag atoms and **(d)** the percentage that is empty space.

Solution

One face of the fcc unit shell can be visualized (Fig. 4.33) as consisting of five Ag atoms describing two right triangles that share a hypotenuse. The hypotenuse, h, is four times the radius of the silver atom. We can use the Pythagorean theorem to evaluate r_{Ag}. The volume of Ag atom is the volume of a sphere of radius r and is given by $(4/3)\pi r^3$. We can use the length of the edge of the unit cell to find its total volume of the unit cell. The volume occupied by the Ag atoms is equal to the number of atoms per unit cell times the volume of each atom. These parameters can be calculated as follows:

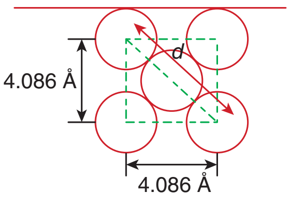


Figure 4.33

(a) The diagonal is given by $d = \sqrt{a^2 + a^2} = \sqrt{2a^2} = \sqrt{2(4.086\ \text{Å})^2} = 5.778\ \text{Å}$

But $d = 4r_{\text{Ag}}$, so, $r_{\text{Ag}} = \dfrac{5.778}{4} = 1.444\ \text{Å}$

(b) The volume of an Ag atom is $(4/3)\pi r_{\text{Ag}}^3$. Substituting, we get

$$V = \frac{4}{3}\pi(1.444\ \text{Å})^3 = 12.61\ \text{Å}^3 = 12.61 \times 10^{-24}\ \text{cm}^3$$

(c) The entire fcc unit cell contains $(4.05 \times 10^{-8})^3 = 66.43 \times 10^{-24}\,\text{cm}^3$ Ag atoms. Each Ag atom has a volume of $1.26 \times 10^{-23}\,\text{cm}^3$. Thus, the volume of four Ag atoms is

$$V_{\text{Ag atoms}} = 4\ \text{Ag atoms} \times \frac{1.261 \times 10^{-23}\ \text{cm}^3}{\text{Ag atom}}$$
$$= 5.044 \times 10^{-23}\ \text{cm}^3$$

For a cubic unit cell, the volume is a^3,

$$V_{\text{unit cell}} = (4.086\ \text{Å})^3 = 68.22\ \text{Å}^3$$
$$= 6.822 \times 10^{-23}\ \text{cm}^3$$

The percentage of the volume of the unit cell occupied by the silver atoms is

$$\%\text{Ag}_{\text{volume}} = \frac{V_{\text{Ag atoms}}}{V_{\text{unit cell}}} \times 100\% = \frac{5.044 \times 10^{-23}\ \text{cm}^3}{6.822 \times 10^{-23}\ \text{cm}^3} \times 100\%$$
$$= 73.9\%$$

(d) So, the percentage empty space = (100 − 73.9) = 26.1%

4.7 | TETRAHEDRAL AND OCTAHEDRAL VOIDS

After packing two layers in hexagonal close packing, we come across two types of voids—tetrahedral and octahedral. This leads to two different types of arrangements. If we cover tetrahedral voids in placing the third layer, we get ABAB… type structure and if we cover octahedral voids, we get ABCABC… type structure.
If there are N atoms/ions in the closed pocked structure, then

1. Number of tetrahedral voids = $2N$
2. Number of octahedral voids = N

Tetrahedral Voids

In the first arrangement, a sphere of the second layer is above the void of the first layer forming a tetrahedral void. The four spheres touch each other in a manner that a tetrahedron is formed when their centers are joined and the space in the center is called a *tetrahedral site/hole* or *void* (indicated by T in Figure 4.34). A tetrahedral void may be represented in a cube as shown in Fig. 4.35.

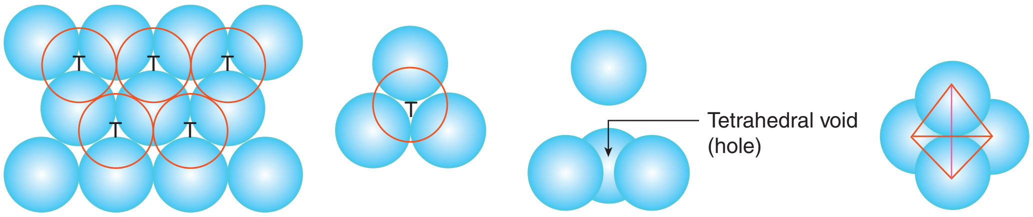


Figure 4.34 Tetrahedral void.

The number of tetrahedral voids per unit cell is eight. *The number of atoms per unit cell in ccp or fcc structure is four and the number of tetrahedral voids is eight, thus the number of voids is twice the number of atoms present in ccp lattice*.

The radius of an tetrahedral void (r) can be calculated in terms of atomic radius (R) as follows: For the convenience of calculation, if the spheres are assumed to occupy the alternate corners of a cube, then the tetrahedral void would lie on the body diagonal of this cube, just touching the spheres on the opposite corners as shown in Fig. 4.35.

Let the length of the side of the cube = a. From right-angled triangle ACB, face diagonal

$$\mathrm{AB} = \sqrt{\mathrm{AC}^2 + \mathrm{BC}^2} = \sqrt{a^2 + a^2} = \sqrt{2}a$$

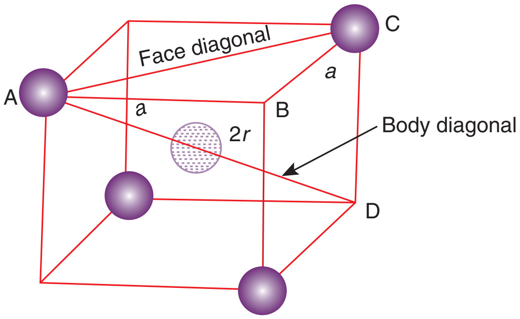


Figure 4.35 Geometrical representation of tetrahedral void.

As spheres A and B are actually touching each other, the face diagonal AB = $2R$. Hence,

$$2R = \sqrt{2}a \quad \text{or} \quad R = \frac{1}{\sqrt{2}}a \tag{4.3}$$

Again from the right-angled triangle ABD, the body diagonal

$$\mathrm{AD} = \sqrt{\mathrm{AB}^2 + \mathrm{BD}^2} = \sqrt{(\sqrt{2}a)^2 + a^2} = \sqrt{3}a$$

But as the smaller sphere in the tetrahedral void touches the bigger spheres along the body diagonal AD = $2(R + r)$,

$$2(R + r) = \sqrt{3}a \Rightarrow R + r = \frac{\sqrt{3}}{2}a \tag{4.4}$$

Dividing Eq. (4.4) by Eq. (4.3), we get

$$\frac{R + r}{R} = \frac{\sqrt{3}a/2}{a/\sqrt{2}} = \frac{\sqrt{3}}{\sqrt{2}}$$

or

$$\frac{r}{R} = \frac{\sqrt{3}}{\sqrt{2}} - 1 = 0.225 \tag{4.5}$$

So, the radius of the tetrahedral void is $r = 0.225\,R$.

Location of Tetrahedral Voids in Face Centered Cubic Structure

In face centered cubic cell, $z_{\mathrm{eff}} = 4 = N$. Therefore,
Number of tetrahedral voids = $2N = 2(4) = 8$
Thus there are eight tetrahedral voids in fcc. To locate these voids, divide the cube into eight equal cubes as shown in Fig. 4.36 (a). Take a small cube out of the eight cubes, then the center of this cube is a tetrahedral void as shown in Fig. 4.36(b). There are two tetrahedral voids on the body diagonal of fcc.

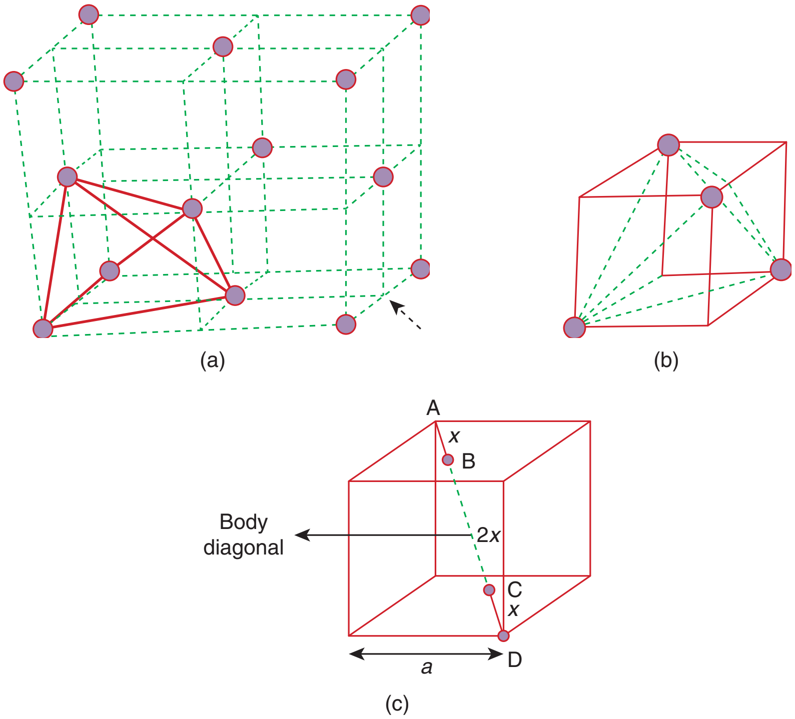


Figure 4.36 (a) Face-centered cubic cell divided into eight cubes with eight tetrahedral voids per unit cell. (b) Small cube with one tetrahedral void in the center. (c) Distance between two tetrahedral voids.

Distance (x) between two tetrahedral voids can be determined from Fig. 4.36 (c) as follows:

$$\mathrm{AD} = \sqrt{3}a = 4x$$

$$2x = \mathrm{BC} = \frac{\sqrt{3}a}{2}$$

$$x = \frac{\sqrt{3}a}{4}$$

Octahedral Voids

In the second arrangement, the triangular voids of the second layer are above the triangular voids of the first layer but their shapes do not overlap. Instead, the apex of one points downwards, whereas that of the other points upwards. As a result *octahedral site/hole* or *void* is formed by six spheres touching each other as shown in Fig. 4.37 (indicated by O).

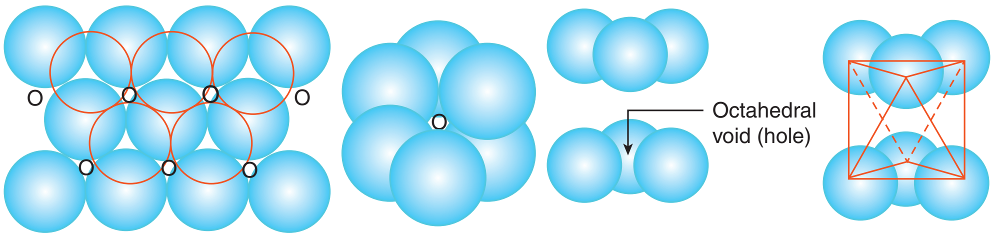


Figure 4.37 Octahedral void.

The contribution of 12 octahedral voids formed on the edges to each unit cell is 12 × 1/4 = 3. The octahedral void at the center of the cube belongs exclusively to that cube; therefore, the total number of octahedral void per unit cell is 3 + 1 = 4. *The number of atoms per unit cell in ccp or fcc structure is four and the number of octahedral voids is four, thus the number of voids is same as the number of atoms present in ccp lattice.*

Note: The number of voids of these two types depends on the number of closely packed spheres. If the number of closely packed spheres is N, then the number of octahedral voids is N and number of tetrahedral voids is $2N$.

The radius of an octahedral void (r) can be calculated in terms of atomic radius (R) as follows:

From the geometry shown in Fig. 4.38:

$$[2(R+r)]^2 (\equiv d^2) = (2R)^2 + (2R)^2$$

or $$4(R+r)^2 = 8R^2 \Rightarrow (R+r)^2 = (2R)^2 \Rightarrow (R+r) = \sqrt{2}R$$

Therefore, $$r = \sqrt{2}R - R = R(\sqrt{2}-1) = R(1.414-1)$$

or $$\frac{r}{R} = 0.414 \qquad (4.6)$$

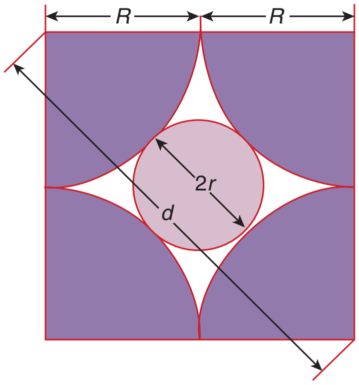


Figure 4.38 Geometrical representation of octahedral void.

The radius of the octahedral void is $r = 0.414\ R$.

Location of Octahedral Voids in Face Centered Cubic Structure

In face centered cubic cell, $z_{\text{eff}} = 4 = N$. Therefore,
Number of octahedral voids $N = 4$
In fcc, octahedral voids are present at the edge center and at the body center (Fig. 4.39). Therefore,

$$\text{Total number of octahedral voids} = \underset{\text{edge centers}}{12} \times \underset{\text{contribution of edge center}}{\left(\frac{1}{4}\right)} + \underset{\text{body center}}{1} \times \underset{\text{contribution of body center}}{(1)} = 4$$

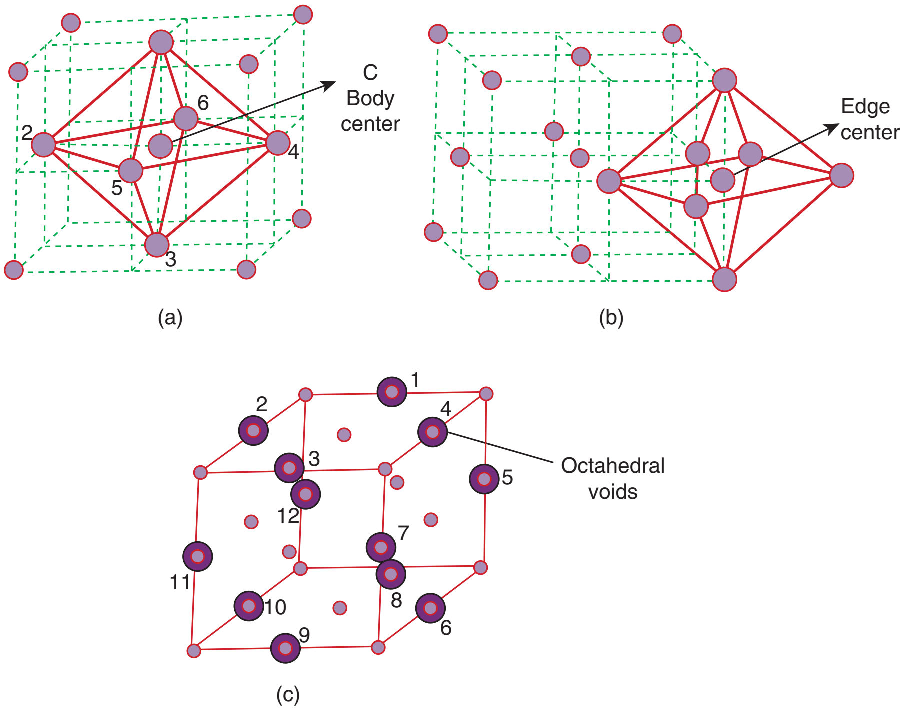


Figure 4.39 Location of octahedral voids in fcc at: (a) body center (b) edge center and (c) 12 octahedral voids as the edge centers.

Formula of a Compound and the Number of Voids Filled

In close-packed structures of ionic compounds, the cations and anions are arranged in a manner so as to maintain electrical neutrality. The cations and anions constituting the ionic compound are usually different. The larger ions form the close-packed structure, whereas the smaller ions are inserted in the voids. Generally, in an ionic crystal the size of anion is bigger than that of cations, so the voids are mostly occupied by the positive metal ions. We know that the number of octahedral voids present in the lattice is the same as number of close-packed particles; whereas the number of tetrahedral voids is twice of that number. It is not essential for all voids to be occupied in an ionic crystal. This number occupied depends on the chemical formula of the compound. On the other hand, if we know the number of voids occupied, we can predict the chemical formula of the compound.

The size and type of void that can be occupied by an ion can be determined by knowing the relative sizes of the cations and anions. The ratio of radius of the smaller ion to that of the bigger ion is known as **radius ratio rule**. On the other hand, if we know the nature of void space, we can predict the radius ratio and identify which ion will occupy the void space.

Solved Example 4-21

In a crystal of an ionic compound, the anion B forms a ccp lattice and the cation A occupies one-half of the tetrahedral voids. What is the formula of the compound?

Solution

In a ccp lattice, the number of tetrahedral voids per atom of the crystal is two. Given that one-half of the tetrahedral voids are occupied, the number of cations is same as the number of anions and hence the formula is AB.

Solved Example 4-22

In a cubic close-packed (ccp) structure of mixed oxide, the lattice is composed of oxide ions, one-fourth of the tetrahedral voids are occupied by divalent metal A and the octahedral voids are occupied by monovalent metal B. What is the formula of the oxide?

Solution

In a ccp structure, total number of octahedral voids is 4 and tetrahedral voids are 8 per unit cell. The lattice is ccp with respect to oxide ions; therefore the number of oxide ions is 4. Given that there are divalent metals ions A in one-fourth of the tetrahedral voids, the number of ions of A is $8 \times 1/4 = 2$. Octahedral voids are occupied by monovalent B metal ions, therefore, the number of ions of B is 4. The formula of the oxide is thus $A_2B_4O_4$ or AB_2O_2.

Solved Example 4-23

In face centered cubic (fcc) crystal lattice, edge length is 400 pm. Find the diameter of the greatest sphere which can be fitted into the interstitial void without distortion of the lattice.

Solution

For fcc, the radius is calculated as

$$r = \frac{a}{2(2)^{1/2}} = \frac{400}{2(2)^{1/2}} = 141.4 \text{ pm}$$

The greatest sphere will fit in octahedral void because it is bigger than tetrahedral void.

Now, radius of the octahedral void (R) = $0.413 \times r = 0.413 \times 141.4 = 58.54$ pm

Therefore, diameter = $2R = 2 \times 58.54 = 117.08$ pm.

Solved Example 4-24

A compound is formed by two elements M and N. The element N forms ccp and atoms of M occupy 1/3rd of tetrahedral voids. What is the formula of the compound?

Solution

The ccp lattice is formed by the atoms of the element *N*. Here, the number of tetrahedral voids generated is equal to twice the number of atoms of the element *N*. According to the question, the atoms of element M occupy 1/3rd of the tetrahedral voids. Therefore, the number of atoms of M is equal to 2 × (1/3) = 2/3rd of the number of atoms of *N*. Therefore, the ratio of the number of atoms of M to that of N is M:N = (2/3): 1 = 2:3. Thus, the formula of the compound is M_2N_3.

4.8 | RADIUS RATIO RULE AND IONIC RADIUS

In close-packed structures of ionic compounds, the cations and anions are arranged in a manner so as to maintain electrical neutrality. The cations and anions constituting the ionic compound are usually different. The larger ions form the close-packed structure, whereas the smaller ions are inserted in the voids. Generally, in an ionic crystal the size of anion is bigger than that of cations, so the voids are mostly occupied by the positive metal ions. We know that the number of octahedral voids present in the lattice is the same as number of close-packed particles; whereas the number of tetrahedral voids is twice of that number. It is not essential for all voids to be occupied in an ionic crystal. This number occupied depends on the chemical formula of the compound. On the other hand, if we know the number of voids occupied, we can predict the chemical formula of the compound.

Thus it can be seen that when the cation size (r) in relation to the size of the anion (R) increases, the coordination number and hence the structure of the crystal changes. That is, for a smaller size of cation, the close-packed structure would be tetrahedral; and when it increases in size it leads to octahedral arrangement and then to body centered cubic close packing of the crystal. This fact is represented in the form of radius ratio rules. The size and type of void that can be occupied by an ion can be determined by knowing the relative sizes of the cations and anions. On the other hand, if we know the nature of void space, we can predict the radius ratio and identify which ion will occupy the void space.

The relationship between the radius, the coordination number and the structural arrangement is called the **radius ratio rule**. The larger the size of the cation, the greater is its coordination number. In other words, the greater is the radius ratio, the greater is its coordination number.

$$\text{Radius ratio} = \frac{\text{Radius of cation } (r)}{\text{Radius of anion } (R)} \quad (4.7)$$

Mathematical Calculation for Critical Radius Ratio

1. For coordination number = 2; the shape of the molecule is linear (Fig. 4.40). Here R is the radius of the anion and r is the radius of the cation.

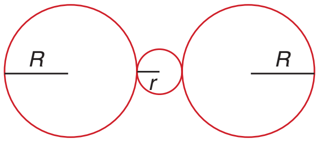


Figure 4.40 Linear molecule with coordination number 2.

If $\frac{r}{R} < 0.155$, then coordination number = 2

2. For coordination number = 3, shape of the molecule is triangular (Fig. 4.41).

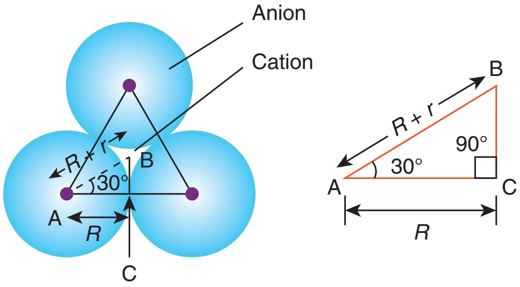


Figure 4.41 Triangular molecule with coordination number 3.

Here,

$$\cos 30^\circ = \frac{R}{R+r}$$

Therefore,

$$\frac{r}{R} = \frac{2}{\sqrt{3}} - 1 = 0.155$$

If $0.155 \le \frac{r}{R} < 0.225$, then coordination number = 3.

3. For coordination number = 4, shape of molecule is tetrahedral (Fig. 4.42).

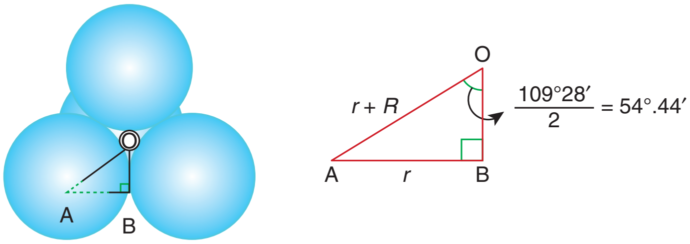


Figure 4.42 Tetrahedral molecule with coordination number 4.

Here,

$$\sin(54^\circ.44') = \frac{r}{r+R}$$

Therefore,

$$\frac{r}{R} = 0.225$$

If $0.225 \le \frac{r}{R} < 0.414$, then coordination number = 4.

4. For coordination number = 6, shape of molecule is octahedral (Fig. 4.43).

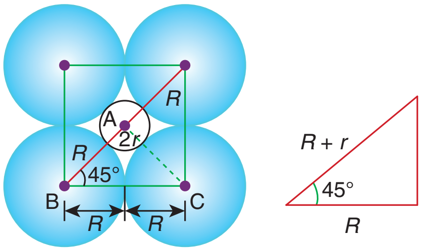


Figure 4.43 Octahedral molecule with coordination number 6.

In Δ OAB, $(R + r)\cos 45° = R$

Therefore, $\dfrac{r}{R} = 1.414 - 1 = 0.414$

If $0.414 \le \dfrac{r}{R} < 0.732$, then coordination number = 6.

5. For coordination number = 8, the shape of molecule is cubic (Fig. 4.44).

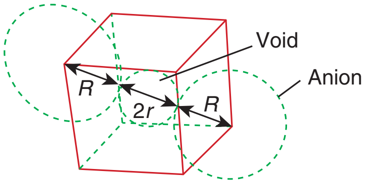


Figure 4.44 Cubic molecule with coordination number 8.

Here,

$$a = 2R$$

$$2(R + r) = \sqrt{3}a$$

Therefore, $\dfrac{r}{R} = 0.732$

If, $0.732 \le \dfrac{r}{R} < 1$, then coordination number = 3.

The radius ratio for important crystal systems is summarized in Table 4.6.

Table 4.6 Radius ratio and coordination number of important crystal structures

Radius ratio	Anions close packing	Coordination number
< 0.155	Linear	2
0.155 to 0.225	Planar triangular	3
0.225 to 0.414	Tetrahedral	4
0.414 to 0.732	Octahedral	6
0.732 to 1.00	Body centered cubic	8

Ionic Radius

Ionic radius is the distance between two oppositely charged ions of the same element. A positive ion is always smaller than the corresponding atom, and the more the number of electrons removed (i.e., the greater the charge on the ion), the smaller the ion becomes.

Atomic radius	Na: 1.86 Å	Fe: 1.17 Å	
Ionic radius	Na^+: 1.02 Å	Fe^{2+}: 0.780 Å (high spin)	Fe^{3+}: 0.645 Å (high spin)

When a negative ion is formed, one or more electrons are added to an atom, the effective nuclear charge is reduced and hence the electron cloud expands. Negative ions are bigger than the corresponding atoms.

Covalent radius, Cl: 0.99 Å	Ionic radius, Cl^-: 1.84 Å

There are several problems in obtaining an accurate set of ionic radii, as a result of which ionic radii are not absolute constants but are approximations. The radius ratio principle is a useful guide, but it is only strictly applicable to ionic compounds. For example, in case of silicates which are partly covalent, the full charge separation to give Si^{4+} and O^{2-} does not occur, and empirical 'effective ionic radii' may be used instead of normal ionic radii. Similarly, though it is possible to measure the internuclear distances in a crystal very accurately by X-ray diffraction. For example, the distance between Na^+ and F^- in NaF, there is no universally accepted formula for apportioning this to the two ions.

Historically, several different sets of ionic radii have been estimated. These are all calculated from observed internuclear distances, but differ in the method used to split the distance between the ions. In measurement of ionic radii, the following need to be taken care:

1. Corrections to these radii are necessary if the charge on the ion is changed.
2. Corrections must also be made for the coordination number and the geometry.
3. The assumption that ions are spherical is probably true for ions from the *s*- and *p*-blocks with a noble gas configuration, but is probably untrue for transition metal ions with an incomplete *d*-shell.
4. In some cases there is extensive delocalization of *d*-electrons, for example, in TiO where they give rise to metallic conduction, or in cluster compounds. This also changes the radii.

Solved Example 4-25

Explain the term ionic radius ratio and its significance in case of ionic crystals. Calculate the ratio for the alkali metal bromides on the basis of the data given below and predict the form of the crystal structure in each case. Ionic radius (in pm) $Li^+ = 74$; $Rb^+ = 148$; $Na^+ = 102$; $Cs^+ = 170$; $K^+ = 138$; $Br^- = 195$.

Solution

If $r^+/r^- = 0.225$, the cation would fit exactly into the tetrahedral voids and have coordination number four. If $r^+/r^- = 0.414$, the cation would fit exactly into the octahedral voids and have coordination number six.

For LiBr, $\frac{r^+}{r^-} = \frac{74}{195} = 0.379$ indicates fcc (Li^+ ions filling alternate tetrahedral voids)

For NaBr, $\frac{r^+}{r^-} = \frac{102}{195} = 0.523$ indicates fcc (Na^+ ions fill all the octahedral voids)

For KBr, $\frac{r^+}{r^-} = \frac{138}{195} = 0.708$ indicates fcc (K^+ ions fill all the octahedral voids)

For RbBr, $\frac{r^+}{r^-} = \frac{148}{195} = 0.76$ indicates bcc (Rb^+ ions fill the body cavity)

For CsBr, $\frac{r^+}{r^-} = \frac{170}{195} = 0.872$ indicates bcc (Cs^+ ions fill the body cavity)

Solved Example 4-26

The radius of Cs^+ is 169 pm and that of Cl^- is 181 pm. Predict the structure of CsCl and the coordination number of Cs^+.

Solution

According to radius ratio rule,

$$\frac{r(Cs^+)}{r(Cl^-)} = \frac{169}{181} = 0.933$$

Since range of $r^+/r^- > 0.732$, the coordination number of Cs^+ is 8 and the structure of CsCl is body centered cubic (bcc).

Solved Example 4-27

Lithium iodide crystal has a face centered cubic unit cell. If the edge length of the unit cell is 620 pm, determine the ionic radius of I^- ion.

Solution

In fcc, face diagonal $= 4r = (a^2 + a^2)^{1/2} = (2)^{1/2}\,a$. Therefore radius is

$$r = (2)^{1/2} \times \frac{a}{4} = 1.414 \times \frac{620}{4} = 219.17 \text{ pm}$$

Solved Example 4-28

If the radius of ions such as Mg^{2+}, Cs^+, O^{2-}, S^{2-} and Cl^- are 0.65, 1.69, 1.40, 1.84, and 1.81 Å, respectively, calculate the coordination numbers of the cations in the crystals of MgS, MgO and CsCl.

Solution

For MgS, the radius ratio is

$$\frac{r_{Mg^{2+}}}{r_{S^{2-}}} = \frac{0.65}{1.84} = 0.353$$

This means tetrahedral structure with coordination number 4.

For MgO, $r_{Mg^{2+}}/r_{O^{2-}} = 0.65/1.40 = 0.464$. This means octahedral structure with coordination number 6.

For CsCl, $r_{Cs^+}/r_{Cl^-} = 1.69/1.81 = 0.934$. This means body centered structure with coordination number 8.

Solved Example 4-29

The ionic radii of Na^+, K^+ and Br^- are 137, 148 and 195 pm, respectively. What are the coordination numbers of cations in KBr and NaBr structures?

Solution

The r^+/r^- ratio is found as follows, from which the geometry and coordination numbers can be predicted:

For NaBr, $r_{Na^+}/r_{Br^-} = 137/195 = 0.703$, it lies in the range of 0.414 to 0.732, the geometry is octahedral and the coordination number is 6.

For KBr, $r_{K^+}/r_{Br^-} = 148/195 = 0.759$, it lies in the range 0.732 to 1.0, the geometry is bcc and the coordination number is 8.

4.9 | SIMPLE IONIC COMPOUNDS

Metals have close packing structures of atoms and hence have high coordination numbers. Ionic solids, however, have lower coordination numbers and can be explained using close packed spheres of ions with the holes in these structures occupied by ions of another kind.

The structures of many ionic solids can be visualized as a close packed arrangement of equivalent negatively charged anions (sometimes the cations) in the fcc or hcp lattices, with the positively charged cations occupying the octahedral and tetrahedral holes in these lattices. We shall look into the crystal structure of some ionic solids in the following subsections.

Rock Salt (or NaCl) Type of Structure

The structure of sodium chloride is based on an fcc arrangement of the larger chloride anions with the sodium cations occupying all the octahedral voids at the body center and edge centers in the fcc lattice. On the other hand, it could also be seen as an fcc packing of sodium ions, with the anions occupying the octahedral voids.

Each of the ions is octahedrally surrounded by six counter ions, and so this structure is called (6,6)-coordination, that is, each Na^+ is surrounded by 6 Cl^- and each Cl^- by 6 Na^+ (Fig. 4.45).

Number of Cl^- ions in each unit cell:
There are 8 Cl^- at the 8 corners and 6 Cl^- at 6 faces. So, the total number of Cl^- ions is

$$(8 \times 1/8) + (6 \times 1/2) = 1 + 3 = 4$$

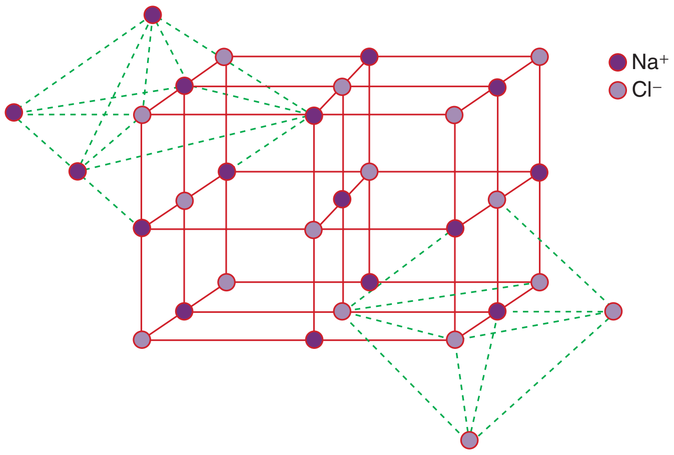


Figure 4.45 Structure of NaCl.

Number of Na^+ ions in each unit cell:
There are 12 Na^+ at the edge centers and 1 Na^+ at the body center. So, the total number of Na^+ ions is

$$12\times(1/4)+1=3+1=4$$

Total NaCl units in one unit cell: 4.

$$\text{Packing fraction}=\frac{4\times\frac{4}{3}\pi\left(r_{Na^+}^3+r_{Cl^-}^3\right)}{8\left(r_{Na^+}+r_{Cl^-}\right)^3}$$

$$\frac{a}{2}=r_{Na^+}+r_{Cl^-}$$

In NaCl, for any anion (placed at the corner):

1. Distance of nearest cation $d=\frac{a}{2}$

   Number of nearest cations = 6
2. Distance of nearest anion $d=\frac{a}{\sqrt{2}}$

   Number of nearest anions = 12
3. Distance of second nearest cation $d=\frac{\sqrt{3}}{2}a$ (body center)

   Number of second nearest cations = 8
4. Distance of second nearest anion $d=a$

   Number of second nearest anions = 6
5. Distance of third nearest cation = $d=\frac{\sqrt{5}}{2}a$ (edge center)

   Number of third nearest cations = 24
6. Distance of third nearest anion $d=\sqrt{\frac{3}{2}}a$ (center of opposite face)

   Number of second nearest anions = 24

Other examples of compounds with the NaCl structure include alkali metal halides (except Cs), ammonium halides, silver halides (except silver iodide) and oxides and sulphides of alkaline earth metals (except BeS).

Sphalerite or Zinc Blende (ZnS) Structure

In this structure, there is an fcc packing of sulphide (S^{2-}) anions at the corners and face centers, and the zinc (Zn^{2+}) cations are present in alternate tetrahedral voids. For each atom in the lattice there are two tetrahedral holes; but according to the stoichiometry of the compound (i.e., same number of cations and anions) only half of them have to be occupied.

The Zn^{2+} cations are tetrahedrally surrounded by S^{2-} anions, and each S^{2-} anion is surrounded by eight tetrahedral sites, of which half are occupied by Zn^{2+} ions, and hence the anions are also four-coordinated. The zinc blende structure, therefore, has (4,4)-coordination (Fig. 4.46).

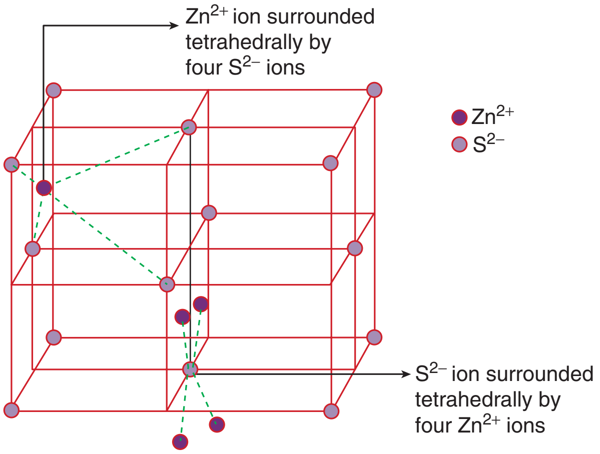

Zn^{2+} ion surrounded tetrahedrally by four S^{2-} ions
● Zn^{2+}
● S^{2-}
S^{2-} ion surrounded tetrahedrally by four Zn^{2+} ions

Figure 4.46 Structure of ZnS.

Number of S^{2-} ions per unit cell: 4.
There are 8 S^{2-} at the corners and 6 S^{2-} at the faces. So, the total number of S^{2-} per unit cell is

$$8\times(1/8)+6\times(1/2)=1+3=4$$

Number of Zn^{2+} ions per unit cell: 4.
Since Zn^{2+} ions occupy only half of the available tetrahedral sites, the number of Zn^{2+} ions per unit cell will be 4.

Total number of ZnS per unit cell: 4.

$$\text{Packing fraction}=\frac{4\times\frac{4}{3}\pi\left(r^3_{Zn^{2+}}+r^3_{S^{2-}}\right)}{\frac{64}{3\sqrt{3}}\left(r_{Zn^{2+}}+r_{S^{2-}}\right)^3}$$

$$\frac{\sqrt{3}a}{4}=r_{Zn^{2+}}+r_{S^{2-}}$$

Other examples of compounds with zinc blende structure include: CuCl, CuBr, CuI, AgI, BeS.

Fluorite Structure (CaF_2)

In this structure, the calcium cations form an fcc lattice, with Ca^{2+} ions at the corners and the face centers, and the fluoride F^- anions occupy all of the tetrahedral voids. For each atom in the fcc array, there are two tetrahedral holes and according to the stoichiometry of the compound both the tetrahedral holes need to be occupied. Thus each F^- anion is tetrahedrally surrounded by 4 Ca^{2+} ions, and each Ca^{2+} cation is surrounded by 8 F^- at tetrahedral sites, all of which are occupied. Hence, the cations are eight-coordinated. So the fluorite structure has (8,4)-coordination (Fig. 4.47). This structure is one of the most common types found in nature.

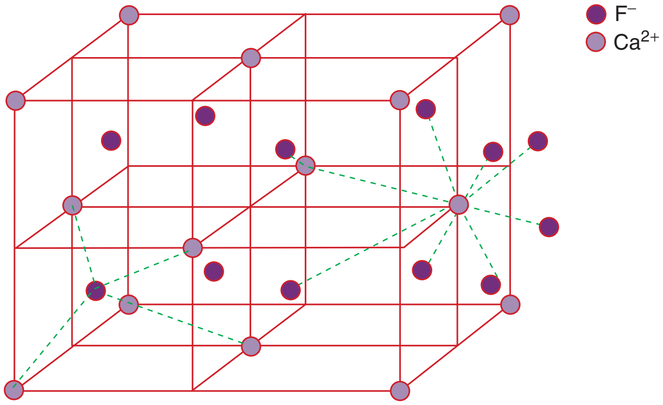


Figure 4.47 CaF_2 structure.

$$\text{Packing fraction}=\frac{4\times\frac{4}{3}\pi\left(r^3_{Ca^{2+}}+2\times r^3_{F^-}\right)}{\frac{64}{3\sqrt{3}}(r_{Ca^{2+}}+r_{F^-})^3}$$

$$\frac{\sqrt{3}a}{4}=r_{Ca^{2+}}+r_{F^-}$$

Other examples of compounds with fluorite structure: BaF_2, $BaCl_2$, SrF_2, $SrCl_2$, etc.

Caesium Chloride (CsCl) Type of Structure

This type of structure is formed when the anion and cation have similar sizes. This is based on a simple cubic lattice of anions with one ion at each of the corners. The cations are located at the center of the anionic cube. The structure can also be considered as a simple cubic array of cations with the anions at the center of the cube. It is an interleaved simple cubic lattice of cations and anions.

Each Cs^+ ion is surrounded by 8 Cl^- ions and each Cl^- ion is surrounded by 8 Cs^+ ions. Therefore, the crystal has (8,8)-coordination (Fig. 4.48). With 8 Cl^- ions at corners contributing one Cl^- and one Cs^+ ion in the body center contributing one Cs^+, it has one CsCl per unit cell.

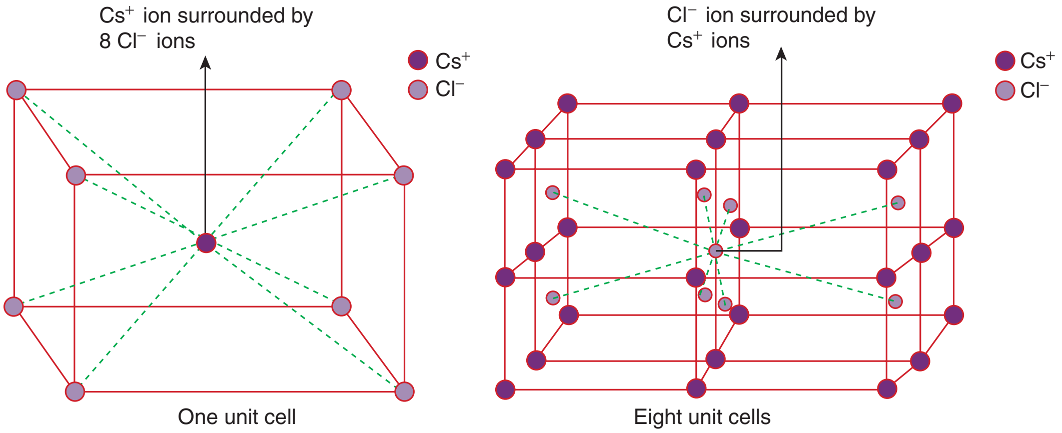

Cs$^+$ ion surrounded by 8 Cl$^-$ ions
Cs$^+$
Cl$^-$
One unit cell
Cl$^-$ ion surrounded by Cs$^+$ ions
Cs$^+$
Cl$^-$
Eight unit cells

Figure 4.48 Structure of CsCl.

$$\text{Packing fraction} = \frac{1 \times \frac{4}{3}\pi(r_{\mathrm{Cs^+}}^3 + r_{\mathrm{Cl^-}}^3)}{\frac{8}{3\sqrt{3}}(r_{\mathrm{Cs^+}} + r_{\mathrm{Cl^-}})^3}$$

$$\sqrt{3}a = 2(r_{\mathrm{Cs^+}} + r_{\mathrm{Cl^-}})$$

Other examples of compounds with caesium chloride type structure include: CsBr, CsI, CsCN, TiCl, TiBr, TiCN, etc.

Perovskite Structure

This structure is adopted by many compounds of the formula ABX_3. In this structure, there is a simple cubic arrangement of B atoms (Ti), with the A atoms (Ca) located at the body center of the cube and the X atoms (O) at the center of the 12 edges of the simple cube.

Thus, the central A ion is surrounded by 12 X ions; the B ion by 6 X ions; and the X ion is linearly coordinated by 2 B ions (Fig. 4.49).

Examples of compounds with Perovskite structure: $NaNbO_3$, $BaTiO_3$, $CaZrO_3$, $YAlO_3$, $KMgF_3$, etc.

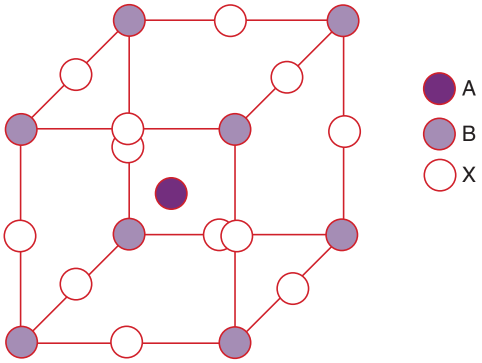


Figure 4.49 Perovskite (ABX_3) structure.

Antifluorite Structure (Na_2O)

The antifluorite structure has the positions of the cations and anions exchanged compared to the fluorite structure, that is, the O^{2-} anions adopt a face centered cubic arrangement with Na^+ cations in the tetrahedral interstices.

The ideal antifluorite would have a cation-to-anion radius ratio of 0.228. However, the ideal ratio is not observed in the antifluorite structure, the observed ratio is higher than the ideal. Each O^{2-} is surrounded by 8 Na^+ ions. Each Na^+ by 4 O^{2-} ions. Na_2O has (4,8)-coordination (Fig. 4.50). Number of Na_2O per unit cell is 4.

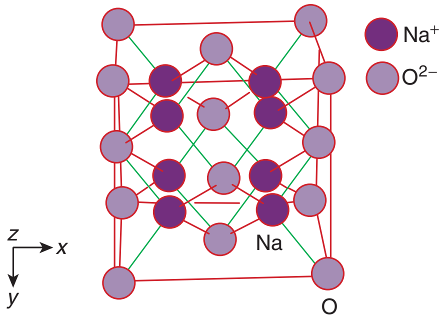


Figure 4.50 Structure of Na_2O.

$$\text{Packing fraction} = \frac{4 \times \frac{4}{3}\pi(2r_{\mathrm{Na^+}}^3 + r_{\mathrm{O^{2-}}}^3)}{\frac{64}{3\sqrt{3}}(r_{\mathrm{Na^+}} + r_{\mathrm{O^{2-}}})^3}$$

$$\frac{\sqrt{3}a}{4} = r_{\mathrm{Na^+}} + r_{\mathrm{O^{2-}}}$$

Antifluorite structure is more commonly found in covalent solids. The alkali metal oxides M_2O (M = Li, Na, K, Rb) crystallize in the antifluorite structure.

Structure of Diamond

In diamond, carbon atoms occupy half of tetrahedral voids and occupy fcc sites (Fig. 3.51)
Number of atoms/unit cell = 8

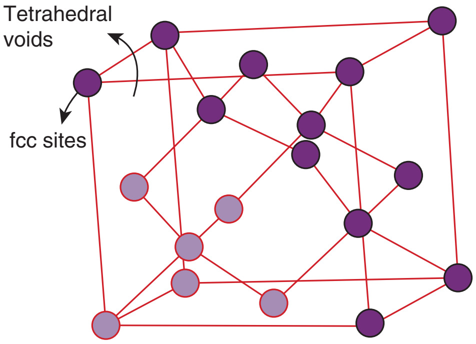


Figure 4.51 Structure of diamond.

The structure of diamond is identical to zinc blende (ZnS) structure, therefore

$$\frac{\sqrt{3}a}{4} = 2r_C$$

Corundum Structure

The general formula for corundum structure is A_2O_3. Some examples of compounds with this structure are: Fe_2O_3, Al_2O_3, Cr_2O_3.
Location of O^{2-} ions = form hcp
Location of A^{3+} ions = $\frac{2}{3}$ of octahedral voids
Since O^{2-} ions form hcp, therefore
z_{eff} of $O^{2-} = 6$
Number of tetrahedral voids = 6 × 2 = 12
Number of octahedral voids = 6 × 1 = 6

$$\text{Packing fraction} = \frac{6\left(\frac{4}{3}\pi r_{O^{2-}}^3\right) + 4\left(\frac{4}{3}\pi r_{A^{3+}}^3\right)}{24\sqrt{2}(r_{O^{2-}})^3}$$

(as volume of hcp = $24\sqrt{2}r^3$)
Therefore, $\frac{2}{3}$ of (6) = 4 = Number of A^{3+} ions
Thus the simplest formula = $A_4O_6 = A_2O_3$

Rutile Structure

In rutile structure, each Ti^{4+} is octahedrally surrounded by 6 O^{2-} ions, whereas each O^{2-} ion is surrounded by only 3 Ti^{4+} ions. These three Ti^{4+}ions are arranged in the three corners of a triangle (Fig. 4.52). Therefore,

Coordination number of Ti^{4+} = 6
Coordination number of O^{2-} = 3

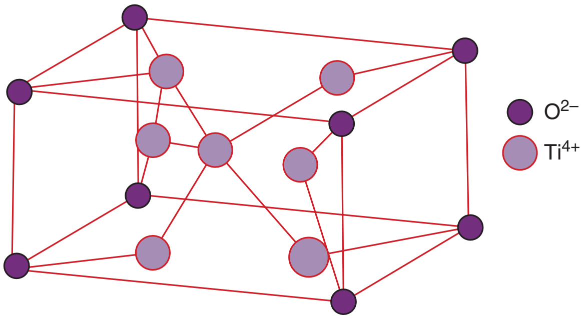


Figure 4.52 Rutile structure.

Note: For a salt A_xB_y, the ratio of coordination numbers is $y : x$. Therefore, formula of rutile is $Ti_3O_6 = TiO_2$

Spinel Structure

In normal spinel structure of general formula AB_2O_4, O^{2-} ions are cubic-closed packed, whereas 1/8th of the tetrahedral holes are occupied by A^{2+} cations and 1/2 of the octahedral holes are occupied by cations B^{3+}. For example, $MgAl_2O_4$, $ZnFe_2O_4$, etc.

Inverse Spinel Structure

General formula = $A^{2+}(B^{2+})_2(O^{2-})_4$
Location of O^{2-} = fcc = 4/unit cell

$$\text{Location of } A^{2+} = \frac{1}{8}(\text{tetrahedral void}) = \frac{1}{8}(8) = 1/\text{unit cell}$$

$$\text{Location of } B^{3+} = \frac{1}{8}(\text{tetrahedral void}) + \frac{1}{4}(\text{octahedral void})$$

$$= \frac{1}{8}(8) + \frac{1}{4}(4) = 2/\text{unit cell}$$

Thus, general formula is $(A^{2+})_1\ (B^{3+})_2\ (O^{2-})_4 = AB_2O_4$

Structure of Oxides of Iron

The structures of different oxides of iron are discussed as follows:

1. In FeO

   Location of O^{2-} = ccp

   Location of Fe^{2+} = All octahedral voids

   (However, actually the oxide is found to $Fe_{0.95}O$ and thus the crystals are Fe- deficient.)

   Number of O^{2-} = 4

   Number of Fe^{2+} = number of octahedral voids = 4

   Therefore, simplest formula is $Fe_4^{2+}O_4^{2-} = FeO$

2. In red brown α- Fe_2O_3

   Location of O^{2-} = hcp

   Location of Fe^{3+} $= \frac{2}{3}$ octahedral voids

   Number of O^{2-} = 6

Number of $Fe^{3+} = \frac{2}{3}(6) = 4$

Therefore, simplest formula is $Fe_4^{3+}O_6^{2-} = Fe_2O_3$

Note: This can also be viewed as if Fe^{2+} ions in FeO are replaced by Fe^{3+} ions. To maintain electrical neutrality, every three ions of Fe^{2+} are to be replaced by two ions of Fe^{3+}

3. In γ- Fe_2O_3 (on oxidation of α-Fe_2O_3)
   Location of O^{2-} = ccp
   Location of Fe^{3+} = randomly distributed in both tetrahedral and octahedral voids.
4. Fe_3O_4 or Magnetite (on heating Fe_2O_3 at 1400 °C)

   $Fe_3O_4 = Fe^{2+}(Fe^{3+})_2O_4$ = Inverse spinel structure

   Location of O^{2-} = fcc = 4 unit/cell

   $$\text{Location of } Fe^{2+} = \frac{1}{8}(\text{tetrahedral voids})$$
   $$= \frac{1}{8}\times(8) = 1\text{ /unit cell}$$
   $$\text{Location of } Fe^{3+} = \frac{1}{8}(\text{tetrahedral voids}) + \frac{1}{4}(\text{octahedral voids})$$
   $$= \frac{1}{8}(8) + \frac{1}{4}(4) = 2\text{/unit cell}$$

   Therefore, simplest structure is $Fe_1^{2+}\,Fe_2^{3+}(O^{2-})_4 = Fe_3O_4$

Solved Example 4-30

KCl crystallizes in the same type of lattice as does NaCl and CsF in the CsCl type of structure, The molar mass of CsF is twice that of KCl and the *a* value for KCl is 1.5 times that of CsF. Calculate the ratio of the density of CsF to that to KCl.

Solution

The relation for KCl is $\frac{a_1^3}{4}\times N_A = \frac{74.5}{\rho_1}$

The relation for CsF is $\frac{a_2^3}{4}\times N_A = \frac{2\times 7.45}{\rho_2}$

Dividing the above two expressions, we get $\frac{a_1^3}{4a_2^3} = \frac{1}{2}\times\frac{\rho_2}{\rho_1}$

Now, $a_1 = 1.5a_2$, so we have

$$\frac{(1.5)^3 a_2^3}{4\times a_2^3} = \frac{1}{2}\times\frac{\rho_2}{\rho_1} \Rightarrow \frac{\rho_2}{\rho_1} = \frac{(1.5)^3}{4}\times 2 = 1.69$$

Solved Example 4-31

If silver iodide crystallizes in a zinc blende structure with I^- ions forming the lattice, then calculate fraction of the tetrahedral voids occupied by Ag^+ ions.

Solution

As I^- ions form the lattice, so the number of tetrahedral voids = 2 *N*. Since there are *N* Ag^+ ions present to occupy these voids. So, the fraction of tetrahedral voids occupied by Ag^+ ions = $N/2N$ = 50%.

Solved Example 4-32

Each rubidium halide crystallizing in the NaCl type lattice has a unit cell length 30 pm greater than for corresponding potassium salt (r_{K^+} = 133 pm) of the same halogen. What is the ionic radius of Rb^+?

Solution

For NaCl type crystal (fcc), $r = a/2(2)^{1/2}$. Now, given that $a_{\text{Rb}^+} = 30 + a_{\text{K}^+}$ and $r_{\text{K}^+} = 133$ ppm.

Now, we know that KCl also crystallizes in fcc structure, hence

$$r_{\text{K}^+} = \frac{a_{\text{K}^+}}{2\sqrt{2}} \Rightarrow a_{\text{K}^+} = r_{\text{K}^+} \times 2\sqrt{2} = 133 \times 2\sqrt{2} = 376.181 \text{ pm}$$

Now, $a_{\text{Rb}^+} = 30 + a_{\text{K}^+} = 30 + 376.181 = 406.181$ pm

Therefore, $r_{\text{Rb}^+} = \dfrac{a_{\text{Rb}^+}}{2\sqrt{2}} \Rightarrow r_{\text{Rb}^+} = \dfrac{406.181}{2\sqrt{2}} = 146.63$ pm

Solved Example 4-33

In spinel structure, O^{2-} ions are cubic-closed packed, whereas 1/8th of the tetrahedral holes are occupied by A^{2+} cations and 1/2 of the octahedral holes are occupied by cations B^{3+}. What is the general formula of this compound?

Solution

Let the number of ions be N.
Then number of tetrahedral voids is $2N$.
The number of octahedral voids is N.
Then A^{2+} occupies one-eighth of tetrahedral voids which means $1/8 \times 2N = (1/4)N$
B^{3+} occupies half of octahedral voids which means $(1/2) \times N = N/2$
Therefore, the formula becomes $1/4N{:}1/2N{:}N = \text{AB}_2\text{O}_4$

Effect of Temperature/Pressure on Crystal Structure

There is a possibility that a given metal may exist in more than one crystal structures. In general, at higher temperatures bcc structure is preferred due to higher entropy. For example, a number of alkali metals exist in bcc form at room temperature. Another example is

$$\underset{\text{Coordination (6:6)}}{\text{NaCl type}} \underset{\text{750 K}}{\overset{\text{High pressure}}{\rightleftharpoons}} \underset{\text{Coordination (8:8}\uparrow}{\text{CsCl type}}$$

Similarly, Fe is in bcc form at room temperature and changes to fcc at 910°C. At higher temperature (1400 °C), it changes to bcc again.

4.10 | X-RAY DIFFRACTION USED TO STUDY CRYSTAL STRUCTURES (BRAGG'S LAW)

The observation of the phenomenon of constructive *wave interference* of X-rays commonly known as X-ray diffraction (XRD) was a direct evidence for the periodic atomic structure of crystals. The internal structure of the crystals in terms of the positional arrangement of atoms/ions and their interatomic spacing are best elucidated using X-rays. In 1913, William Lawrence Bragg and his father William Henry Bragg observed that crystalline solids reflect X-rays and produce intense peaks of specific patterns. The Braggs were awarded the Nobel Prize in physics in 1915 for their work in determining crystal structures of crystals such as NaCl, ZnS and diamond. Their work has resulted in establishing a relation between the wavelength of the X-rays (which is of the same order as interatomic distances, *viz*., 10^{-8}cm) and the spacing between the lattice planes.

When a crystal is bombarded with X-rays at a certain incident angle, the crystal acts as diffraction grating and produces an intense reflected beam. This occurs when the diffracted beam leaves the crystal at an angle equal to that of incidence and the wavelengths of the scattered X-rays interfere constructively. In order for the waves to interfere constructively, the differences in the travel path must be equal to integral multiples of the wavelength. The experimental setup for Bragg's experiment is shown in Fig. 4.53:

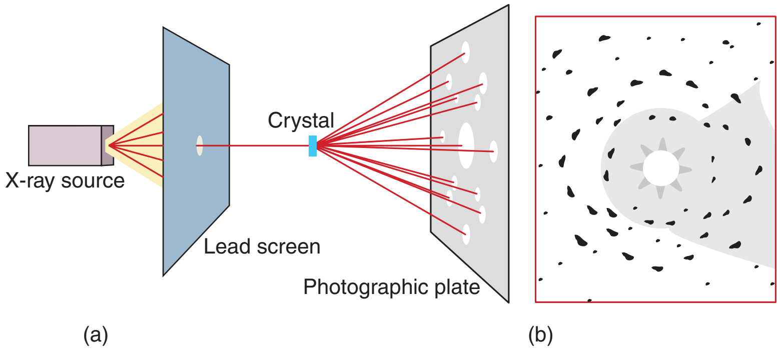


Figure 4.53 Experimental setup for X-ray diffraction study.

Diffraction of X-rays by the crystal for constructive interference can be explained as follows:

A crystal can be considered as being made up of parallel equidistant atomic planes, represented by lines AB, CD and EF as shown in Fig. 4.54.

Two beams (Y and Z) of the X-ray which are in phase, fall on the surface of the crystal. Suppose ray Y gets reflected from atoms in the first lattice plane AB and ray Z is reflected from the second layer of atoms on plane CD. Then the rays Y and Z will be in phase after reflection only if the difference in distance travelled by the two rays (QR + RS) equals an integral number of wavelength ($n\lambda$), for constructive interference.

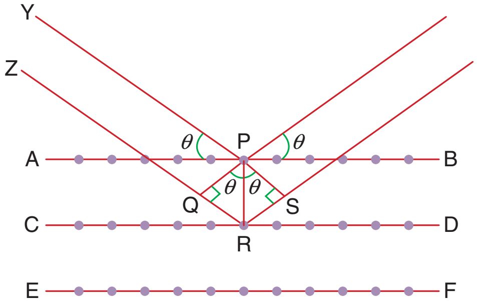


Figure 4.54 X-ray diffraction by a crystal.

That is to say that $$\text{QR} + \text{RS} = n\lambda \tag{4.8}$$

From the figure, $$\text{QR} = \text{RS} = \text{PR}\sin\theta \tag{4.9}$$

Therefore, $$\text{QR} + \text{RS} = 2\,\text{PR}\sin\theta$$

If the distance between the successive atomic planes is d, then,

$$\text{PR} = d \tag{4.10}$$

So, from Eqs. (4.8)–(4.10), $$n\lambda = 2d\sin\theta \tag{4.11}$$

This is Bragg's equation or the law relating wavelength of the incident X-ray, the distance between the atomic layers and the angle of diffraction; where n is an integer $(1, 2, 3, 4, \ldots)$ representing the serial order of diffracted beams.

Bragg's equation can be used to calculate the distances between repeating planes of the particles in a crystal. Similarly, if interplanar distances are given, the corresponding wavelengths of the incident X-ray beam can be calculated. A given unknown crystal is expected to have many planes of atoms in its structure; therefore, the collection of "reflections" of all the planes can be used to identify an unknown crystal.

Although Bragg's law uses the interference pattern of X-rays scattered by crystals, diffraction using any beam, like ions, electrons, neutrons and protons, with a wavelength similar to the interatomic or intermolecular distance in structures can be used to study the structure of all states of matter.

Miller Indices for Crystallographic Planes in Cubic Unit Cells

The Miller indices are conventions used to specify directions and planes in a crystal plane. These are defined as the reciprocal of the fractional intercepts, which the plane makes with the crystallographic x-, y- and z-axes of the three non-parallel edges of the cubic unit cell. The procedure for determining the Miller indices involves the following steps:

1. Choose a plane that does not pass through the origin (0, 0, 0).
2. Determine the intercepts of the plane in terms of the crystallographic x-, y- and z-axes for a unit cube. These intercepts may be fractions.
3. Find the reciprocals of these intercepts.
4. Clear the fractions and determine the smallest set of whole numbers which are in the same ratio as the intercepts. These whole numbers are the Miller indices of crystallographic planes and are enclosed in parentheses without using comma. The notation (hkl) is used to indicate Miller indices, where h, k and l are Miller indices of cubic crystal plane for x-, y- and z-axes.

For simple cubic crystals, the lattice vectors are orthogonal and of equal length, denoted by lattice constant a. For these structures, the spacing between adjacent (hkl) lattice planes is given by

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \tag{4.12}$$

For example, consider the Miller indices for:

1. Simple cubic structure as shown in Fig. 4.55.

$$d_{100} = \frac{a}{\sqrt{1^2 + 0^2 + 0^2}} = a$$

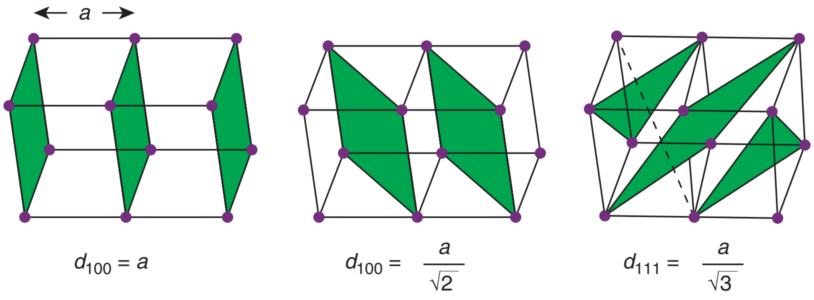

a
$d_{100} = a$
$d_{100} = \frac{a}{\sqrt{2}}$
$d_{111} = \frac{a}{\sqrt{3}}$

Figure 4.55 Miller indices in simple cubic structure.

2. Face centered cubic structure as shown in Fig. 4.56.

$$d_{200} = \frac{a}{\sqrt{2^2 + 0^2 + 0^2}} = \frac{a}{2}$$

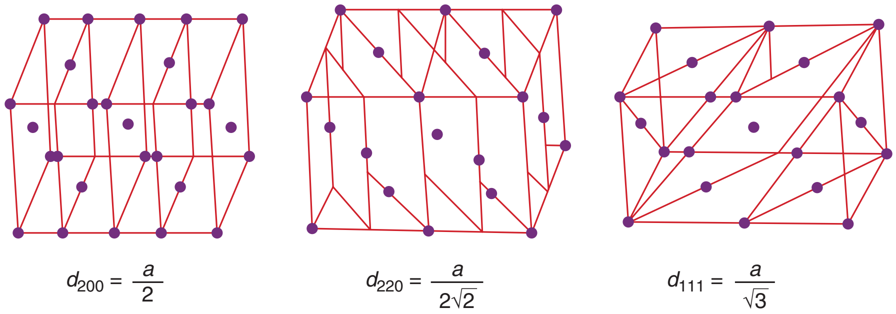

$d_{200} = \frac{a}{2}$
$d_{220} = \frac{a}{2\sqrt{2}}$
$d_{111} = \frac{a}{\sqrt{3}}$

Figure 4.56 Miller indices in face centered cubic structure.

Solved Example 4-34

What are the Miller indices of a plane with intercepts $0.5a$, $0.25b$ and $1.5c$?

Solution

Miller indices are found as

$$\frac{1}{0.5}:\frac{1}{0.25}:\frac{1}{1.5}=2:4:\frac{2}{3}=6:12:2=3:6:1.$$

Solved Example 4-35

X-rays of wavelength 0.154 nm striking an aluminium crystal, get reflected at an angle 19.3° showing first-order diffraction. Calculate the spacing between the plane of aluminium atoms in pm.

Solution

According to Bragg's equation, $n\lambda = 2d\sin\theta$ where n is order of reflection, λ is wavelength, θ is angle of reflection. Given that $n=1$, $\lambda = 0.154$ nm $= 154$ pm and $\theta = 19.3°$. Therefore,

$$d=\frac{n\lambda}{2\sin\theta}=\frac{1\times 154}{2\sin 19.3°}=\frac{154}{2\times 0.435}=177\,\text{pm}$$

Solved Example 4-36

At what glancing angle would the first-order diffraction occur, when copper radiation ($\lambda = 154$ pm) interacts with lattice planes that are 154 pm apart.

Solution

According to Bragg's law, $n\lambda = 2d\sin\theta$. Given that $n=1$, $d=154$ pm, $\lambda = 154$ pm. Therefore,

$$1\times 154 = 2\times 154\sin\theta$$

or

$$\sin\theta = 0.5 \Rightarrow \theta = 30°$$

Solved Example 4-37

X-ray diffraction measurements reveal that copper crystallizes with a face centered cubic lattice in which the unit cell length is 3.62 Å. What is the radius of a copper atom expressed in angstroms and in picometers?

Solution

In Fig. 4.57, we see that copper atoms are in contact along a diagonal (the dashed line below) that runs from one corner of a face to another corner.

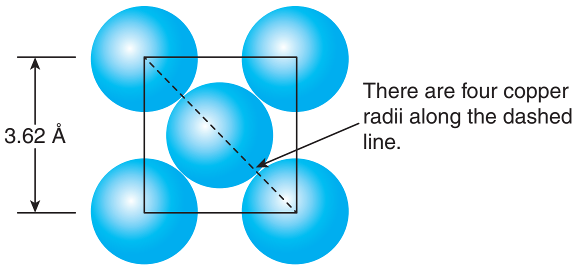


Figure 4.57

From geometry, the length of the diagonal is $\sqrt{2}$ times the length of the edge of the unit cell.

$$\text{Diagonal} = \sqrt{2}\times(3.62\text{ Å}) = 512\text{ Å}$$

If we call the radius of the copper atom r_{Cu}, then the diagonal equals $4\times r_{\text{Cu}}$. Therefore,

$$4\times r_{\text{Cu}} = 5.12\text{ Å} \Rightarrow r_{\text{Cu}} = 1.28\text{ Å}$$

The calculated radius of the copper atom is 1.28 Å. Next we convert this to picometers.

$$1.28\times\frac{1\times 10^{-10}}{1}\times\frac{1}{1\times 10^{-12}}=128\text{ pm}$$

Solved Example 4-38

Copper metal crystallizes with fcc structure. The density of the crystal 2698 kg m^{-3} and mass is 26.98 kg. X-rays of wavelength 0.1537 nm are diffracted by the crystal and the Bragg's angle is 19.2°. Identify the crystal plane (in terms or its Miller indices) which caused this diffraction.

Solution

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}}$$

Substituting values, we get

$$2698 = \frac{26.98 \times 4}{a^2 \times 6.023 \times 10^{23}}$$

$$a^3 = \frac{26.98 \times 4}{2698 \times 6.023 \times 10^{23}}$$

$$= 6.6412 \times 10^{-26} \text{ m}^3$$

or $$a = 4.05 \times 10^{-9} \text{ m}$$

Now, $\lambda = 2d\sin\theta$. Substituting values, we get 0.1537 = $2d$ sin19.2°

$$d = \frac{0.1537}{2 \times 0.3289} = 0.2336 \text{ nm}$$

This is the distance between the planes in the crystals, causing diffraction

$$a = \frac{d_{\text{hkl}}}{\sqrt{h^2 + k^2 + l^2}}$$

Therefore, $$\sqrt{h^2 + k^2 + l^2} = \frac{a}{d_{hkl}} = \frac{0.4046}{0.2336} = 1.732$$

or $$h^2 + k^2 + l^2 = (1.732)^2 = 3$$

Hence, the crystal plane (111) is causing diffraction.

4.11 | DEFECTS IN CRYSTALS

Defect refers to a disruption in the periodic order of a crystalline material. These occur in crystals because they lower the energy of a crystal to make it more thermodynamically stable. Defects are also known as imperfections in solids and are classified on the basis of the irregularity in arrangement of electrons as electronic imperfections; based on geometry as atomic imperfections; and based on the ratio of anions and cations as stoichiometric defects.

The atomic imperfections in solids are further classified as follows:

1. **Point defects:** In these defects, also known as zero-dimensional point defects, there are points where an atom is missing or is irregularly placed in the lattice structure. These include vacancy, interstitial and substitutional atoms.
   - **(a) Vacancy:** A vacant lattice position in which the atom is missing. It is created when a solid is formed.
   - **(b) Interstitial:** This defect occurs when an atom occupies a position other than its normal lattice position. The atom in the interstitial may be of the same type as the other atoms of the crystal (self-interstitial) or an impurity atom. Interstitial impurity atoms are much smaller than the atoms in the host matrix and fit into the open space between the host atoms of the lattice structure. One example of interstitial impurity is carbon added to iron to make steel. Carbon atoms (radius of 0.071 nm) fit nicely in the spaces between the larger (0.124 nm) iron atoms.
   - **(c) Substitutional:** A substitutional impurity is an atom of a different type than the host lattice atom, which replaces one of the bulk atoms in the lattice. Size of these atoms is generally closer to the host atom. One example of substitution impurity is presence of zinc atoms in brass, where zinc atoms (radius of 0.133 nm) replace some of the copper atoms (radius of 0.128 nm).
2. **Line defects:** These defects, also known as single dimensional or linear defects, are groups of atoms in irregular positions. Linear defects are commonly called *dislocations*.

The number and type of defects in a crystal can be varied and controlled. Defects may be desirable or undesirable and they have a profound effect on material properties. Defects are studied using optical microscopy, scanning electron microscopy, transmission electron microscopy, X-ray diffraction, etc.

Types of Point Defects

Point defects are imperfect point-like regions in the crystal. Their typical size is about 1–2 atomic diameters. These defects could be due to vacancies and interstitials and include lattice vacancies, self-interstitial atoms, substitution impurity atoms and interstitial impurity atoms. Due to the presence of both vacancies and interstitial types of defects, there is a change in the coordination and hence an imbalance in the forces around the atoms of defect as compared to other atoms in the solid. This results in distortion of the lattice around the defect (Fig. 4.58).

Based on their nature, these are classified into three types: stoichiometric defects, impurity defects and non-stoichiometric defects.

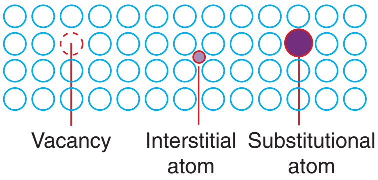


Figure 4.58 Three types of point defects.

1. **Stoichiometric defects:** Stoichiometric compounds are those where the numbers of the different types of atoms or ions present are exactly in the ratios indicated by their chemical formulae. At one time these were called Daltonide compounds, in contrast to Berthollide or non-stoichiometric compounds where the chemical composition of a compound was variable, not constant. They obey the law of constant composition that *the same chemical compound always contains the same elements in the same composition by weight*.

   At absolute zero, crystals tend to have a perfectly ordered arrangement. As the temperature increases, the amount of thermal vibration of ions in their lattice sites increases, and if the vibration of a particular ion becomes large enough, it may jump out of its lattice site. This constitutes a point defect. The higher the temperature, the greater the chance that lattice sites may be unoccupied. Since the number of defects depends on the temperature, they are sometimes called **thermodynamic defects**.

   The following two defects can be shown by **non-ionic solids**.

   (a) Vacancy defects: These result when some of the lattice sites in the crystal are vacant. These defects develop during formation of crystals or when the substance is heated. Since the number of particles per unit area is reduced, the density of the solid decreases as a result of vacancy defect.

   (b) Interstitial defects: These arise when some constituent particles (atoms or molecules) occupy interstitial sites in the crystal. Since the number of particles per unit area is more than in a regular crystal, the density of the solid increases as a result of interstitial defect.

   In **ionic crystals**, point defects must satisfy the condition of charge neutrality. There are two possibilities for intrinsic point defects in ionic solids. Two types of defects observed in stoichiometric ionic compounds are called Frenkel and Schottky defects. A consequence of these defects is that a crystalline solid that has defects may conduct electricity to a small extent. Electrical conductivity in a chemically pure, stoichiometric semiconductor is called "*intrinsic semiconduction*". In the above cases, intrinsic semiconduction occurs by an ionic mechanism. If an ion moves from its lattice site to occupy a "hole", it creates a new "hole". If the process is repeated many times, a "hole" may migrate across a crystal, which is equivalent to moving a charge in the opposite direction. The density of a defect lattice should be different from that of a perfect lattice. The presence of "holes" should lower the density, but if there are too many "holes" there may be a partial collapse or distortion of the lattice—in which case the change in density is unpredictable. The presence of ions in interstitial positions may distort (expand) the lattice and increase the unit cell dimensions.

   (a) Frenkel defect: When an ion is displaced from its regular position to an interstitial position, it creates a vacancy; this pair of vacancy–interstitial is called *Frenkel defect*. This defect consists of a vacant lattice site (a "hole"), and the ion which ideally should have occupied the site now occupies an interstitial position [see Fig. 4.59(a)].

   Metal ions are generally smaller than the anions. Thus it is easier to squeeze A^+ into alternative interstitial positions, and consequently it is more common to find the positive ions occupying interstitial positions. This type of defect is favored by a large difference in size between the positive and negative ions, and consequently the coordination number is usually low (4 or 6). Examples of this type of defect are ZnS, AgCl, AgBr and AgI. This defect is also known as dislocation defect and does not result in any change in density of the substance.

   The number of defects formed is relatively small, and at room temperature NaCl has only one defect in 10^{15} lattice sites, this value rising to one in 10^6 sites at 500°C and one in 10^4 sites at 800°C.
   Number of Frankel defects can be determined as

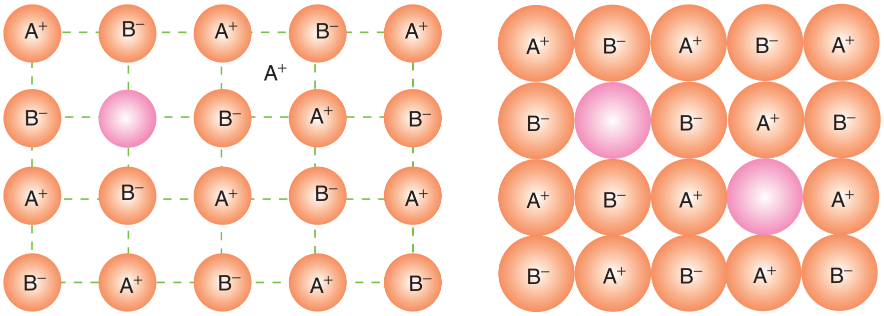
$$n = \left(\frac{N}{N_i}\right)^{1/2} e^{-E/2kT}$$

where n = number of Frenkel defects
N = number of ions in the ionic crystal
N_i = number of interstitial sites
E = Energy required to create n Frenkel defects

T = Temperature
k = Boltzmann constant

Note: The fraction of the surface of crystal vacancies is given by

$$\frac{n}{N} = e^{-E/RT}$$



(a) (b)

Figure 4.59 (a) Frenkel defect. (b) Schottky defect.

(b) Schottky defect: When a pair of one cation and one anion of equal valence is missing from an ionic crystal, the condition of charge neutrality is still maintained. The pair of vacant sites, thus formed, is called *Schottky defect* [Fig. 4.59(b)]. These *ion–pair vacancies* decrease density of the solid and facilitate atomic diffusion. This type of defect is shown by highly ionic compounds, which have high coordination number and small difference in the sizes of cations and anions. Some ionic compounds exhibiting Schottky defect are NaCl, KCl, KBr, AgBr and CsCl. Some compounds like AgBr show both Frenkel and Schottky defects.

Number of Schottky defects can be determined as

$$n = Ne^{-E/2kT}$$

where n = Number of Schottky defects
N = Number of ions in the ionic crystal
E = Energy required to create these Schottky defects
T = Temperature
k = Boltzmann constant $= \dfrac{R}{N_A} = 1.38 \times 10^{23}\ \text{JK}^{-1}$

2. Impurity defects: Defects in ionic crystals can be introduced by adding impurities in which the ions are in different valence state than the constituent ions of the crystal. For example, if small amounts of calcium chloride ($CaCl_2$) are added to sodium chloride (NaCl), some Ca^{2+} ions replace Na^+ ions and occupy the sites earlier occupied by Na^+. Then in order to maintain the electrical neutrality of the crystal, one Na^+ leaves the lattice, thus effectively each Ca^{2+} replaces two Na^+ ions. A cation vacancy is thus generated in the lattice, which is equal to the number of Ca^{2+} ions added. The crystal lattice so obtained is a solid solution of NaCl and $CaCl_2$ (Fig. 4.60).

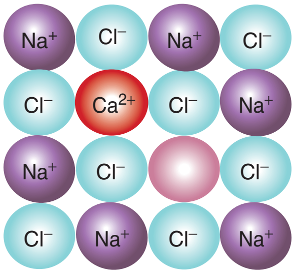


Figure 4.60 Impurity defect.

3. Non-stoichiometric defects: In non-stoichiometric or Berthollide compounds, the ratio of the number of atoms of one kind to the number of atoms of the other kind does not correspond exactly to the ideal whole number ratio implied by the formula. Such compounds do not obey the law of constant compositions. There are many examples of these compounds, particularly in the oxides and sulphides of the transition elements. Thus, in FeO, FeS or CuS the ratio of Fe:O, Fe:S or Cu:S differs from that indicated by the ideal chemical formula. If the ratio of atoms is not exactly 1:1 in the above cases, there must be either an excess of metal ions, or a deficiency of metal ions (e.g., $Fe_{0.84}O$–$Fe_{0.94}O$, $Fe_{0.9}S$). Electrical neutrality is maintained either by having extra electrons in the structure, or changing the charge on some of the metal ions. This makes the structure irregular in some way, that is, it contains defects, which are in addition to the normal thermodynamic defects already discussed. These defects are mainly of two types—(a) metal excess defect and (b) metal deficient defect.

(a) Metal excess defect: Crystals with metal excess defect contain free electrons, and if these migrate they conduct an electric current. Since there are only a small number of defects, there are only a few free electrons that can conduct electricity. Thus the amount of current carried is very small compared with that in metals, fused salts or salts in aqueous solutions. Materials with these defects are called *semiconductors.* Since the mechanism is normal electron conduction, these are called *n-type semiconductors*. These free electrons may be excited to higher energy levels giving absorption spectra, and in consequence their compounds are often colored, example, non-stoichiometric form of NaCl is yellow, that of KCl is lilac, and of ZnO is white when cold but yellow when hot.

This may occur in two different ways:

- **Metal excess defect due to anionic vacancies:** In these defects, a negative ion may be absent from its lattice site, leaving a “hole” which is occupied by an electron, thereby maintaining the electrical balance [(see Fig. 4.61(a)]. This is rather similar to a Schottky defect in that there are ‘holes’ and not interstitial ions, but only one ‘hole’ is formed rather than a pair. This type of defect is formed by crystals which would be expected to form Schottky defects. When compounds such as NaCl, KCl, LiH or δ-TiO are *heated with excess of their constituent metal vapors*, or treated with high energy radiation, they become deficient in the negative ions, and their formulae may be represented by $AX_{1-\delta}$ where δ is a small fraction. The non-stoichiometric form of NaCl is yellow, and that of KCl is blue—lilac in color. Note the similarity with the flame colorations for Na and K.

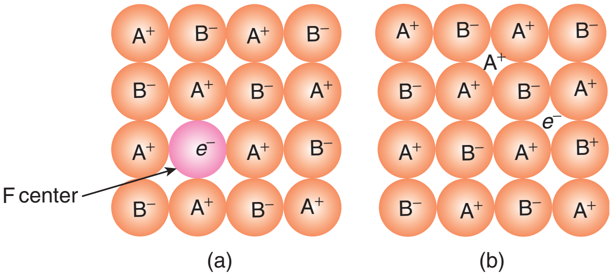


Figure 4.61 Metal excess defects because of (a) absent anion, (b) interstitial cations.

The crystal lattice has vacant anion sites, which are occupied by electrons. Anion sites occupied by electrons in this way are called *F*-centers. (*F* is an abbreviation for *Farbe*, the German word for color.) These *F*-centers are associated with the color of the compound and the more *F*-centers present, the greater the intensity of the coloration. Solids containing *F*-centers are paramagnetic, because the electrons occupying the vacant sites are unpaired.

- **Metal excess defect due to the presence of extra cations in the interstitial sites:** Metal excess defects also occur when an extra positive ion occupies an interstitial position in the lattice, and electrical neutrality is maintained by the inclusion of an interstitial electron [see Fig. 4.61(b)]. Their composition may be represented by the general formula $A_{1+\delta}X$.

  This type of defect is rather like a Frenkel defect in which ions occupy interstitial positions, but there are no “holes”, and there are also interstitial electrons. This kind of metal excess defect is much more common than the first, and is formed in crystals which would be expected to form Frenkel defects (i.e., the ions are appreciably different in size, have a low coordination number, and have some covalent character). For example, ZnO, CdO, Fe_2O_3 and Cr_2O_3.

(b) Metal deficiency defect: Metal-deficient compounds may be represented by the general formula $A_{1-\delta}X$. Crystals with metal deficiency defects are semiconductors. Suppose the lattice contains A^+ and A^{2+} metal ions. If an electron ‘jumps’ from an A^+ ion to the positive center (an A^{2+} ion), the original A^+ becomes a new positive center. There has been an apparent movement of A^{2+}. With a series of similar ‘hops’, an electron may be transferred in one direction across the structure, and at the same time the positive hole migrates in the opposite direction across the structure. This is called positive hole, or *p-type semiconduction*. In principle, metal deficiency can occur in two ways. Both the ways require the metal to exhibit variable valence, which is mainly shown by transition metals.

- **Positive ions absent:** If a positive ion is absent from its lattice site, the charges can be balanced by an adjacent metal ion having an extra positive charge [see Fig. 4.62(a)]. Examples of this are FeO, NiO, δ-TiO, FeS and CuI. (If an Fe^{2+} is missing from its lattice site in FeO, then there must be two Fe^{3+} ions somewhere in the lattice to balance the electrical charges. Similarly, if a Ni^{2+} is missing from its lattice site in NiO, there must be two Ni^{3+} present in the lattice.)

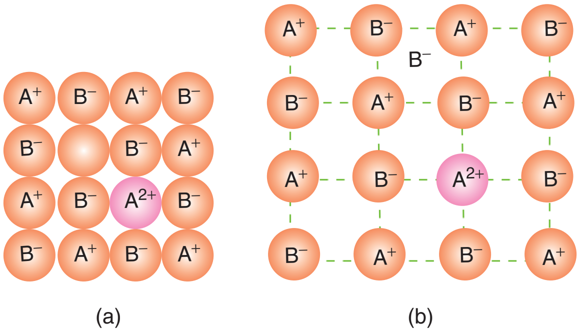


Figure 4.62 Metal deficiency caused by (a) missing positive ion and (b) interstitial negative ions.

- **Extra interstitial negative ions:** In principle it might be possible to have an extra negative ion in an interstitial position and to balance the charges by means of an extra charge on an adjacent metal ion [see Fig. 4.62(b)]. However, since negative ions are usually large, it would be difficult to fit them into interstitial positions. No examples of crystals containing such negative interstitial ions are known at present.

Solved Example 4-39

The crystal AB (rock salt structure) has molecular weight 6.023y amu where y is an arbitrary number in amu. If the minimum distance between cation and anion is $y^{1/3}$ nm and the observed density is 20 kg m^{-3}. Find the (a) density in kg m^{-3} and (b) type of defect. **(IIT-JEE 2004)**

Solution

(a) The edge length of unit cell, $a = 2\times y^{1/3}$ nm. Given that $M = 6.023y$ g mol^{-1} $= 6.023y\times10^{-3}$ g mol^{-1}.

For rock salt structure, $z = 4$. Therefore, density is

$$\rho = z\times\frac{M}{a^3\times N_A}$$

$$=\frac{(4\times6.023\times10^{-3}\,y\text{ kg mol}^{-1})}{(2\times y^{1/3}\times10^{-9}\text{ m})^3\times6.023\times10^{23}\text{ mol}^{-1}}$$

$$= 5\text{ kg m}^{-3}$$

(b) As the observed density > calculated density, it means that some impurity or extra metal ion is present in interstitial sites. Hence, the defect is interstitial defect or metal excess defect.

Solved Example 4-40

An element crystallizes in fcc lattice having edge length 400 pm. Calculate the maximum diameter of atom which can placed in interstitial site without distorting the structure. **(IIT-JEE 2005)**

Solution

In face centered cubic arrangement (fcc), the interstitial sites will be octahedral and tetrahedral voids.

For octahedral voids, $r_1/r_2 = 0.414$ (radius ratio for coordination number 6)

For tetrahedral voids, $r_1/r_2 = 0.225$ (radius ratio for coordination number 4)

where r_1 is the radius of atom in interstitial sites and r_2 is the radius of atom arranged in fcc.

$$4r_2 = \sqrt{2}\,a$$

For maximum diameter of atom in interstitial site, octahedral sites will be considered (since they are bigger than tetrahedral voids). Then

$$\text{Diameter} = 2r_1 = 2(0.414\ r_2)$$

$$= \frac{2\times 0.414\times 400}{2\sqrt{2}} = 117.1 \text{ pm}$$

Solved Example 4-41

Analysis shows that nickel oxide has the formula $Ni_{0.98}O_{1.00}$. What fractions of the nickel exist as Ni^{2+} and Ni^{3+} ions?

Solution

From the valence numbers, it is clear that three Ni^{2+} are equivalent to two Ni^{3+} ions. So, three Ni^{2+} ions would be replaced by two Ni^{3+} ions. In other words, when two Ni^{3+} ions replace three Ni^{2+} ions, then there is a net loss of Ni^{2+} ions from the formula.

The total loss of Ni from one molecule of NiO = (1 – 0.98) = 0.02

Therefore, the total Ni^{3+} ions present in one molecule O of NiO = 2 × 2.02 = 0.04

The total number of Ni^{2+} and Ni^{3+} ions in one molecule of NiO = 0.98

So, out of 0.98 atoms of Ni, only 0.04 atoms are present as Ni^{3+}. Therefore,

$$\text{Percentage of Ni as } Ni^{3+} = \frac{0.04}{0.98}\times 100 = 4.1\%$$

Thus, 4.1% of the total Ni in $Ni_{0.98}O$ is present as Ni^{3+}. Hence, the percentage of Ni present as $Ni^{2+=}$ 100 – 4.1 = 95.9%.

Solved Example 4-42

If NaCl is doped with 10^{-3} mol% of $SrCl_2$, what is the concentration of cation vacancies?

Solution

For every Sr^{2+} ion introduced in NaCl crystal, two Na^+ ions are removed to maintain electrical neutrality. One lattice site occupied by Sr^{2+} ion and the other remains vacant. Hence a cationic vacancy is created in NaCl by doping with $SrCl_2$. Since by the addition of one Sr^{2+} ion, one cationic vacancy is created, therefore by the addition of 10^{-3} mol of Sr^{2+} ion 10^{-3} mol% of cationic vacancy will be created. Hence 1 mol% of a substance contains 6.023×10^{23} atoms/molecules/ions/vacancies.

Therefore, 10^{-3} mol% of cationic vacancy =

$$\frac{6.023\times 10^{23}\times 10^{-3}}{100} = 6.023\times 10^{18}$$

4.12 | ELECTRICAL PROPERTIES OF SOLIDS

Solids may be classified in terms of their conductivity as conductors, insulators or semiconductors.

1. **Conductors:** These are solids with conductivities ranging from 10^4 to 10^7 $\text{ohm}^{-1}\text{m}^{-1}$. Metals are good conductors and have conductivity in the range 10^7 $\text{ohm}^{-1}\text{m}^{-1}$.
2. **Insulators:** These are solids with very low conductivity, generally in the range 10^{-20} to 10^{-10} $\text{ohm}^{-1}\text{m}^{-1}$. Non-metals and substances like rubber and wood are insulators.
3. **Semiconductors:** These are solids with conductivity that is intermediate between conductors and insulators and lies in the range 10^{-6} to 10^4 $\text{ohm}^{-1}\text{m}^{-1}$. Germanium and silicon are examples of semiconductors.

Conduction of Electricity in Metals

The mobile electrons account for the high thermal and electrical conduction of metals. If one end of a piece of metal is heated, electrons at that end gain energy and move to an unoccupied molecular orbital where they can travel rapidly to any other part of the metal, which in turn becomes hot. In an analogous manner, electrical conduction takes place through a minor disturbance in energy promoting an electron to an unfilled level, where it can move readily. In the absence of an electric field, equal numbers of electrons will move in all directions. If a positive electrode is placed at one end, and a negative electrode at the other, then electrons will move towards the anode much more readily than in the opposite direction; hence an electric current flows.

Metals conduct electricity in solid as well as molten state and the conductivity is related to the number of valence electrons and can be explained using the band theory. According to the band theory:

1. Atomic orbitals of the metal atoms form molecular orbitals that are so closely spaced that instead of having discrete energies, the available energy states form bands.
2. The essential criteria for any solid to conduct are the presence of electrons in conduction band and the gap between the valence and conduction band.
3. In metals, the valence band overlaps the conduction band, in semiconductors there is a small enough gap between the valence and conduction bands that thermal or other excitations can bridge the gap and in insulators the electrons in the valence band are separated by a large gap from the conduction band.

In electrical conductors (metals), either the valence band is only partly full, or the valence and conduction bands overlap. There is, therefore, no significant gap between filled and unfilled MOs, and perturbation can occur readily. In insulators (non-metals), the valence band is full, so perturbation within the band is impossible, and there is an appreciable difference in energy (called the band gap) between the valence band and the next empty band. Electrons cannot therefore be promoted to an empty level where they could move freely (Fig. 4.63).

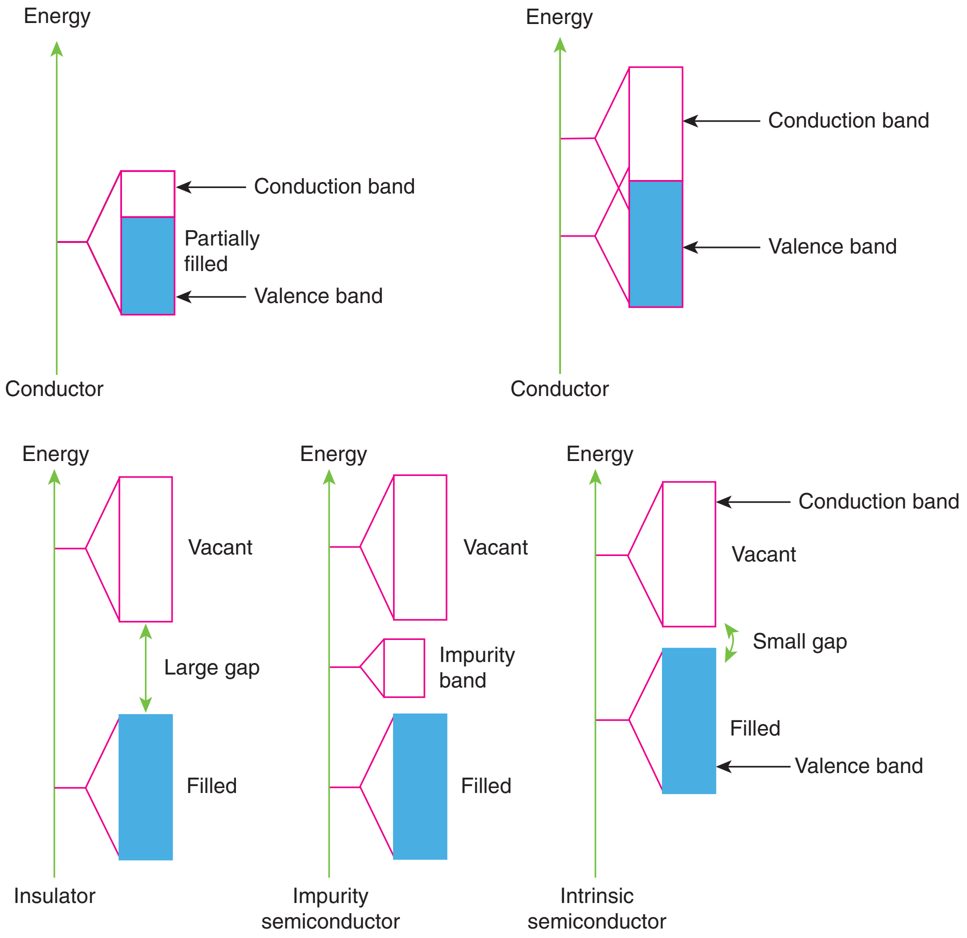


Figure 4.63 Conductors, insulators, impurity and intrinsic semiconductors.

Conduction of Electricity in Semiconductors

Semiconductors are solids where there is only a small difference in energy, called a *band gap*, between the filled valence band of electrons and a conduction band. If cooled to absolute zero, the electrons occupy their lowest possible energy levels. The conduction band is empty, and the material is a perfect insulator. At normal temperatures, some electrons are thermally excited from the valence band to the conduction band, and hence they can conduct electricity by the passage of electrons at normal temperatures. Both the promoted electron in the conduction band and the unpaired electron left in the valence band can conduct electricity. The conductivity is in between that of a metal and an insulator and depends on the number of electrons in the conduction band.

The conductivity of semiconductors increases with temperature, because the number of electrons promoted to the conduction band increases as the temperature increases. Both n-type and p-type semiconductors are produced by doping an insulator with a suitable impurity. The band from the impurity lies in between the valence and conduction bands in the insulator, and acts as a bridge, so that electrons may be excited from the filled valence band of the insulator to the empty conduction band of the impurity, or vice versa.

Pure semiconductor grade silicon needs to be incorporated with impurities for it to develop semiconductor properties. This process is known as **doping** and a number of doping techniques are used. The process of doping introduces electronic defects in the solids and makes them conducting. Doping may be carried out using impurities which are either *electron rich* or *electron deficient* as compared to the intrinsic semiconductor. Germanium and, to an even greater extent, silicon are the most important commercial examples of semiconductors. The crystal structures of both are like diamond. Atoms of Si and Ge both have four electrons in their outer shell, which form four covalent bonds to other atoms. In both Si and Ge at very low temperatures, the valence band is filled and the conduction band is empty. Under these conditions, Si and Ge are both insulators, and cannot carry any electric current.

1. **Electron-rich impurities:** Pure Si and Ge can be made semiconducting in a controlled way by adding electron-rich impurities which act as charge carriers. Si or Ge are first obtained extremely pure by zone refining. Some atoms with five outer electrons, such as arsenic As (or any Group 15 element), are added to the silicon crystal. A minute proportion of Si atoms are randomly replaced by As atoms with five electrons in their outer shell. Only four of the outer electrons on each As atom are required to form bonds in the lattice. At absolute zero or low temperatures, the fifth electron is localized on the As atom. However, at normal temperatures, some of these fifth electrons on As are excited into the conduction band, where they can carry current quite readily. This is **extrinsic conduction**, and it increases the amount of semiconduction far above that possible by intrinsic conduction. Since the current is carried by excess electrons, it is ***n*-type semiconduction**.
2. **Electron-deficient impurities:** Alternatively a crystal of pure Si may be doped with some atoms with only three outer electrons (Group 13 elements), such as indium In. Each indium atom uses its three outer electrons to form three bonds in the lattice, but they are unable to form four bonds to complete the covalent structure. One bond is incomplete, and the site normally occupied by the missing electron is called a "positive hole". At absolute zero or low temperatures, the positive holes are localized around the indium atoms. However, at normal temperatures a valence electron on an adjacent Si atom may gain sufficient energy to move into the hole. This forms a new positive hole on the Ge atom. The positive hole seems to have moved in the opposite direction to the electron. By a series of "hops", the "positive hole" can migrate across the crystal. This is equivalent to moving an electron in the opposite direction, and thus current is carried. Since current is carried by the migration of positive centers, this is ***p*-type semiconduction**.

Note: Intrinsically silicon and germanium conduct a small current. However, the addition of a small amount of dopant atoms into their regular crystal lattice produces dramatic change in their electrical properties, producing n-type and p-type semiconductors.

Purified silicon (or germanium) crystals can be converted to p-type or n-type semiconductors by high temperature diffusion of the appropriate dopant element, up to a concentration of 1 part in 10^8. In principle, any of the Group 13 elements boron, aluminium, gallium or indium can be used to make p-type semiconductors, though indium is the most used because of its low melting point. Similarly, Group 15 elements such as phosphorus or arsenic can be used to make n-type semiconductors, but because of its low melting point arsenic is most used. Some important examples of compounds with Group 13 and Group 15 elements are InSb, GaAs, AlP, etc. A large number of semiconductors have also been prepared by combination with Group 12 and Group 16 elements, for example, ZnS, CdS, CdSe and HgTe.

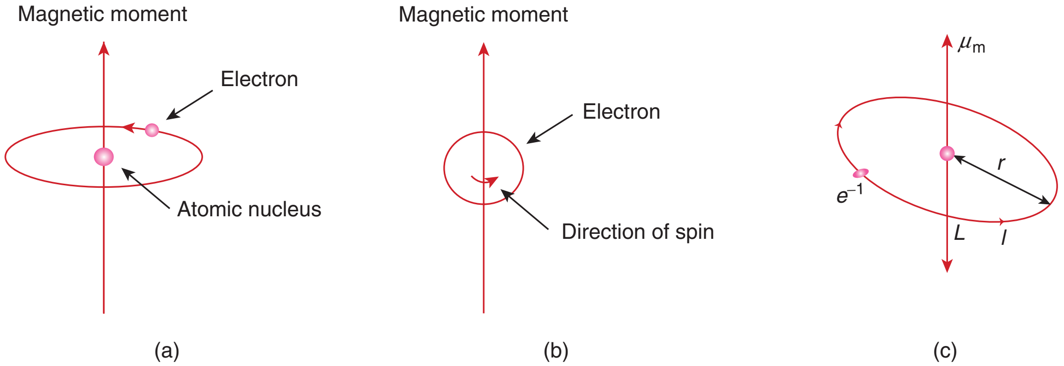
Transition metal oxides show a wide range values for electrical conductivity. At one extreme are oxides like MnO which are insulators and at the other extreme are oxides like ReO_3, CrO_2, RuO_2, TiO and NbO which show metal-like conductivities. In between there are a number of oxides that exhibit semiconductor properties, such as Nb_2O_5 and

SnO_2. Conduction in oxides can be ionic or electronic. The oxides which show semiconductor to metal transitions or semiconductor to insulator transitions are of special interest and find many applications. These include V_2O_3, VO_2, VO_3, Ti_2O_3, TiO_3, etc.

Superconductors offer no resistance to the flow of current. They are derived from *p*-block elements as they become superconducting at room temperature. At 2–5 K, most of the metals become superconductors. However, complex oxides become superconductors at higher temperatures. For example, the oxide $Tl_2Ca_2Ba_2Cu_3O_{10}$ becomes superconducting at 125 K, that is, it offers no resistance to the flow of electric current.

4.13 | MAGNETIC PROPERTIES OF SOLIDS

On an atomic scale, individual atoms cause magnetic fields because each electron in an atom behaves like a tiny magnet. Its magnetic moment originates from two types of motions: (a) its orbital motion around the nucleus [Figs. 4.64(a) and (b)] its spin around its own axis [Fig. 4.64(b)].



(a) (b) (c)

Figure 4.64 Diagrammatic representation of magnetic moment associated with (a) motion of electron in an orbit and (b) spin of electron around its own axis. (c) Angular momentum vector of an electron producing the current.

Each orbit is assumed to be a loop of electric current (I). As per the electromagnetic theory, a loop of current produces a magnetic field, and hence it is not surprising that the electrons in an atom also generate a magnetic field. Therefore, an electric current loop can act like a magnetic dipole of moment.

$$\mu_m = I\,A$$

Here I is the current and A is the area of the loop, and such current flows counter-clockwise relative to an observer standing along the direction of the magnetic moment [Fig. 4.64(c)]. The dipole direction is perpendicular to the plane of the loop. The magnitude of this magnetic moment is very small. It is expressed in terms of Bohr magneton, which is equal to 9.27×10^{-24} Am^2. Solids can be classified into the following five categories based on the magnetic behavior shown by them:

1. **Diamagnetism:** Such substances are weakly magnetized in a direction opposite to that of an applied magnetic field. Substances showing diamagnetism do not have any unpaired electrons. Since all the electrons are paired, the magnetic moment caused by spin of one electron is canceled by the other and net magnetic moment is zero. Some examples of diamagnetic materials include NaCl, KCl, TiO_2, etc. A diamagnetic substance is weakly repelled when placed near a magnet. Diamagnetism is independent of temperature.
2. **Paramagnetism:** Such substances are magnetized along the direction of the applied magnetic field. They are weakly attracted by the applied magnetic field. The substances showing paramagnetism contain one or more unpaired electrons and can be of the following types:
   - **(a)** All those atoms and molecules, which have an odd number of electrons, are paramagnetic. Such a system, according to quantum mechanics, cannot have zero total spin; therefore, each atom or molecule has a net magnetic moment, which arises from the electron spin angular momentum. Organic free radicals and gaseous nitric oxide are some materials that exhibit paramagnetism.

- **(b)** All free atoms and ions with unfilled inner electron shells, and many of these ions, when in solid or in solution, are paramagnetic. Some well-known examples are $KMnO_4$, Na, K, Cu^{2+} and Fe^{3+} ions. Paramagnetism is shown by these substances only in the presence of a magnetic field.

3. **Ferromagnetism:** Such substances are strongly attracted by applied magnetic field and can be permanently magnetized. These materials exhibit a phenomenon of spontaneous magnetization. At sufficiently high temperatures, all these substances become *paramagnetic*. Atomic magnetic moments, in ferromagnetic materials, arise when the electrons of an atom possess a net magnetic moment due to their angular momentum. The metal atoms are grouped together in small regions called domains and each domain acts as a tiny magnet. These domains are randomly oriented in an unmagnetized portion of the substance. However, in presence of an applied field, these domains get aligned with the applied magnetic field and the combined effect of the atomic magnetic moments gives rise to a relatively large magnetization for a given applied field. These ordered domains continue to exist even when the external magnetic field is removed and the ferromagnetic substance becomes a permanent magnet. Examples are iron, nickel, cobalt $CrO_{2,}$ etc. This is a temperature dependent property.
4. **Antiferromagnetism:** In such materials, the dipoles have equal moments, but adjacent dipoles point in opposite directions. Thus, the moments balance each other, resulting in a zero net magnetization. The atomic magnetic moments, at sufficiently low temperatures form an ordered array, which alternates or spirals so as to give no net total moment in zero applied magnetic field. Antiferromagnetism is exhibited by some metals, alloys and salts of transition elements such as MnO, MnSe, etc.
5. **Ferrimagnetism:** In such materials, the atomic dipoles are arranged antiparallel to one another and the number of magnetic moments aligned in one direction is more than that aligned in the other direction. As a result magnetic moment in one direction has a larger magnitude and a *net* magnetization is observed which is does not disappear. Such materials are weakly attracted by magnetic fields. These lose ferrimagnetism on heating and become paramagnetic. The most versatile of ferrimagnetic systems are substances like Fe_3O_4, and ferrites like $MgFe_2O_4$ and $ZnFe_2O_4$.

4.14 | DIELECTRIC PROPERTIES OF SOLIDS

Insulators or dielectrics are materials used to prevent the loss of electricity through certain parts in an electrical system. Dielectrics also store electrical charges. When the main function is that of insulation, the materials are called *insulators* and when the charge storage is the main function, they are called *dielectrics*. On applying electric field, polarization of charge takes place leading to formation of dipoles (containing nucleus and electron clouds at the extreme ends). In some cases, permanent dipoles could be formed which cause the crystal to have net dipole moment by aligning themselves in an ordered manner. The following properties are shown by polar crystals:

1. **Piezoelectricity:** The electricity produces due to application of mechanical stress causing deformation and displacement of ions. The crystals are called piezoelectric crystals and examples include lead zirconate, quartz, etc.
2. **Pyroelectricity:** Small electric current produced on heating piezoelectric crystals generates pyroelectricity.
3. **Ferroelectricity:** When in piezoelectric crystals having permanent polarized dipoles even in the absence of the electric field, on applying field the direction of polarization changes. This phenomenon is called ferroelectricity, the crystals are called ferroelectric crystals. Examples include Rochelle's salt, potassium hydrogen phosphate, barium titanate, etc.
4. **Antiferroelectricity:** In some crystals, the dipoles point alternately in upward and downward direction. Thus, the net dipole moment of the crystal is zero. These crystals are called antiferroelectric. Examples include lead zirconate, etc.

SOLVED OBJECTIVE QUESTIONS FROM PREVIOUS YEAR PAPERS

1. The pycnometric density of sodium chloride crystal is 2.165×10^3 kg m^{-3} while its X-ray density is 2.178×10^3 kg m^{-3}. The fraction of the unoccupied sites in sodium chloride crystal is **(IIT-JEE 2003)**

(A) 5.96
(B) 5.96×10^{-2}
(C) 5.96×10^{-1}
(D) 5.96×10^{-3}

Solution

(D) We know that $\text{density} = \dfrac{\text{mass}}{\text{volume}}$

Thus, $\text{volume} = \dfrac{\text{mass}}{\text{density}}$

$$\text{Hence, pycnometric volume} = \frac{M}{2.165 \times 10^3}\,\text{m}^3$$

$$\text{and} \qquad \text{X-ray volume} = \frac{M}{2.178 \times 10^3}\,\text{m}^3$$

Volume unoccupied = Pycnometric volume − X-ray volume

$$= \frac{M}{10^3}\left[\frac{1}{2.165} - \frac{1}{2.178}\right] = \frac{0.013\,M \times 10^{-3}}{2.165 \times 2.178}$$

Fraction of volume unoccupied

$$= \frac{0.013\ \text{M} \times 10^{-3}/2.165 \times 2.178}{\text{M} \times 10^{-3}/2.165} = 5.96 \times 10^{-3}$$

2. Which of the following fcc structures contains cations in the alternate tetrahedral voids? **(IIT-JEE 2005)**

(A) Na_2O (B) ZnS
(C) CaF_2 (D) CaO

Solution

(B) In ZnS, anions (S^{2-}) are placed in fcc manner and cations (Zn^{2+}) are placed in alternate tetrahedral voids.

3. Match the crystal system/unit cells mentioned in Column I with their characteristic features mentioned in Column II.

Column I	Column II
(A) Primitive cubic and face centered cubic	(p) Have these cell parameters $a = b = c$ and $\alpha = \beta = \gamma$
(B) Cubic and rhombohedral	(q) Are two crystal systems
(C) Cubic and tetragonal	(r) Have only two crystallographic angles of 90°
(D) Hexagonal and monoclinic	(s) Belong to same crystal system

(IIT-JEE 2007)

Solution

$A \rightarrow (p, s); B \rightarrow (p, q); C \rightarrow (q); D \rightarrow (q, r).$

4. **Statement 1:** Band gap in germanium is small.
Statement 2: The energy spread of each germanium atomic energy level is infinitesimally small. **(IIT-JEE 2007)**

(A) Statement 1 is True, Statement 2 is True; Statement 2 is a correct explanation for Statement 1.
(B) Statement 1 is True, Statement 2 is True; Statement 2 is NOT a correct explanation for Statement 1.
(C) Statement 1 is True, Statement 2 is False.
(D) Statement 1 is False, Statement 2 is True.

Solution

(C) A semiconductor has only small difference in energy between the filled valence band and empty conduction band. The energy gap between valence and conduction band for germanium is 68 kJ mol^{-1} at room temperature. In order to increase its conduction, doping is done.

5. Read the following paragraph and answer the questions that follow:

Paragraph for Questions 5a–5c: In hexagonal systems of crystals, a frequently encountered arrangement of atoms is described as a hexagonal prism. Here, the top and bottom of the cell are regular hexagons and three atoms are sandwiched in between them. A space-filling model of this structure called hexagonal closed packed (hcp) is constituted of a sphere on a flat surface surrounded in the same plane by six identical spheres as closely as possible. Three spheres are then placed over the first layer so that they touch each other and represent the second layer. Finally, the second layer is covered with a third layer that is identical to the bottom layer in relative position. Assume radius of every sphere to be *r*. **(IIT-JEE 2008)**

5a. The number of atoms in this hcp unit cell is

(A) 4 (B) 6
(C) 12 (D) 17

Solution

(B) 12 × 6 (corners) + 2 × (1/2) (at face centers) + 3 (in the body center) = 6

5b. The volume of this hcp unit cell is

(A) $24\sqrt{2}\,r^3$ (B) $16\sqrt{2}\,r^3$
(C) $12\sqrt{2}\,r^3$ (D) $\dfrac{64}{3\sqrt{3}}r^3$

Solution

(A) Volume of unit cell = base × height
Base area of regular hexagon $= 6 \times (3)^{1/2}/4 \times (2r)^2$
$= 6 \times (3)^{1/2} r^2$
Volume of unit cell $= 6(3)^{1/2} r^2 + 4r\,(2/3)^{1/2} = 24(2)^{1/2} r^3$

5c. The empty space in this hcp unit cell is

(A) 74% (B) 47.6%
(C) 32% (D) 26%

Solution

(D) Volume occupied in hcp arrangement = 74%, so the empty space is 26%.

6. The correct statement(s) regarding defects in solids is (are)

(A) Frenkel defect is usually favored by a very small difference in the sizes of cation and anion.
(B) Frenkel defect is a dislocation defect.
(C) Trapping of an electron in the lattice leads to the formation of F-center.
(D) Schottky defects have no effect on the physical properties of solids. **(IIT-JEE 2009)**

Solution

(B), (C). Frenkel defects occur in compounds in which the anions are much larger in size than cations. It is a dislocation effect. The presence of Schottky defects lowers the density of the crystal (means it affects the physical properties of the crystal). In the metal excess defects, the electron is trapped in anion vacancies known as F-centers.

7. The coordination number of Al in the crystalline state of $AlCl_3$ is ________. **(IIT-JEE 2009)**

Solution

(6) Coordination number of Al is 6. It exists in ccp lattice with 6 coordinate layer structure.

8. Silver (atomic weight = 108 mol^{-1}) has a density of 10.5 $g\,cm^{-3}$. The number of silver atoms on a surface of area 10^{-12} m^2 can be expressed in scientific notation as $y \times 10^x$. The value of x is ________. **(IIT-JEE 2010)**

Solution

We know that density = mass/volume where density = 10.5 g cm^{-3}. This means 10.5 g of Ag is present in 1 cm^3.

The number of atoms of Ag present in 1 cm^3 = $10.5/108 \times N_A$

In 1 cm, number of atoms of Ag = $(10.5/108 \times N_A)^{1/3}$

In 1 cm^2, number of atoms of Ag = $(10.5/108 \times N_A)^{2/3}$

In 10^{-8} cm^2, number of atoms of Ag = $(10.5/108 \times N_A)^{2/3} \times 10^{-8} = (1.05 \times 6.022 \times 10^{24}/10^8) \times 10^{-8} = 1.5 \times 10^7$.

Hence, $x = 7$.

9. The packing efficiency of the two-dimensional square unit cell shown in Fig. 4.65 is ________. **(IIT-JEE 2010)**

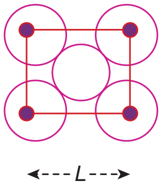


Figure 4.65

(A) 39.27% (B) 68.02%
(C) 74.05% (D) 78.54%

Solution

(D) $a = (2(2)^{1/2}\, r)$. Hence the packing efficiency

$$= \frac{2 \times \pi r^2}{(2\sqrt{2}r)^2} = \frac{2\pi r^2}{8r^2} = \frac{\pi}{4} \times 100 = 78.5\%.$$

10. The number of hexagonal faces that are present in a truncated octahedron is ________. **(IIT-JEE 2011)**

Solution

(6) This can be seen in Fig. 4.66.

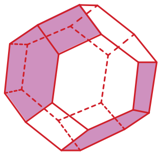


Figure 4.66

11. A compound M_pX_q has cubic close packing (ccp) arrangement of X. Its unit cell structure is shown in Fig. 4.67. The empirical formula of the compound is

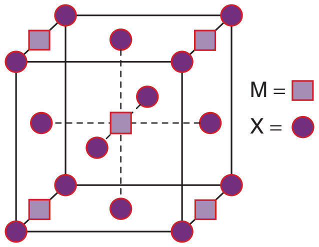


Figure 4.67

(A) MX (B) MX_2
(C) M_2X (D) M_5X_{14} **(IIT-JEE 2012)**

Solution

(B) As X is present at the corners of the cube and also at the faces of the cube, so the contribution of X will be

$$8(\text{corners}) \times \frac{1}{8} \times (\text{contribution of each corner atom})$$
$$+\, 6(\text{faces}) \times \frac{1}{2}(\text{contribution of each face}) = 4$$

As M is present at the body center and at each diagonal, so its contribution will be

$$4(\text{diagonals}) \times \frac{1}{4}(\text{contribution of each diagonal}) +$$
$$1(\text{body center}) = 2$$

So, the unit cell formula becomes M_2X_4 and the empirical formula will be MX_2.

12. The arrangement of X^- ions around A^+ ion in solid AX is given in the Fig. 4.68 (not drawn to scale). If the radius of X^- is 250 pm, the radius of A^+ is **(JEE Advanced 2013)**

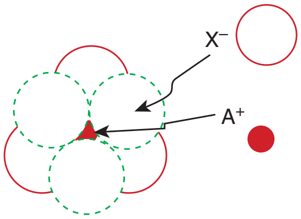


Figure 4.68

(A) 104 pm (B) 125 pm
(C) 183 pm (D) 57 pm

Solution

(A) From Fig. 4.68, it can be seen that the cation A^+ occupies octahedral void formed by the anion X^-. The radius ratio for an octahedral void is $r_{A^+}/r_{X^-} = 0.414$. Now, given that the radius of anion X^- is 250 pm, so the radius of A^+ is

$$r_{A^+} = 0.414 \times 250 = 103.50 \simeq 104 \text{ pm}$$

13. If the unit cell of a material has cubic close packed (ccp) array of oxygen atoms with ***m*** fraction of octahedral holes occupied by aluminum ions and ***n*** fraction of tetrahedral holes occupied by magnesium ions, ***m*** and ***n***, respectively, are **(JEE Advanced 2015)**

(A) $\frac{1}{2}, \frac{1}{8}$ (B) $1, \frac{1}{4}$

(C) $\frac{1}{2}, \frac{1}{2}$ (D) $\frac{1}{4}, \frac{1}{8}$

Solution

(A) For ccp lattice; number of atoms (z) = 4

Number of octahedral and tetrahedral holes is 4 and 8 respectively.

From the balance of charge on the salt, we have $4O^{2-}$ give charge of –8, which is balanced by $2Al^{3+}$ and 1 Mg^{2+} or a charge of +8. Therefore, the formula is Al_2MgO_4.

Al^{3+} is present in $\frac{2}{4} = \frac{1}{2}$ of the octahedral holes

Mg^{2+} are present in $\frac{1}{8}$ of the tetrahedral holes

14. How many unit cells are present in a cube-shaped ideal crystal of NaCl of mass 1 g? **(AIEEE 2003)**

(A) 2.57×10^{21} unit cells (B) 5.14×10^{21} unit cells

(C) 1.28×10^{21} unit cells (D) 1.71×10^{21} unit cells

Solution

(A) 1 unit cell has 4 NaCl. So, mass of one unit cell is

$$4 \times \frac{58.5}{6.023} \times 10^{23} \text{ g}$$

Number of unit cells in one gram is

$$\frac{1}{4} \times \frac{1}{58.5 \times 6.02 \times 10^{23}} = 2.57 \times 10^{21}$$

15. Glass is a

(A) microcrystalline solid. (B) supercooled liquid.

(C) gel. (D) polymeric mixture.

(AIEEE 2003)

Solution

(B) This is because it has the property to flow.

16. What type of crystal defect is indicated in Fig. 4.69? **(AIEEE 2004)**

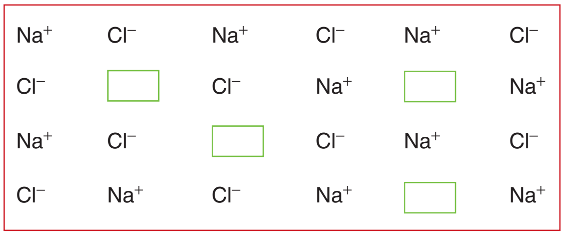

Na^+ Cl^- Na^+ Cl^- Na^+ Cl^-
Cl^- ☐ Cl^- Na^+ ☐ Na^+
Na^+ Cl^- ☐ Cl^- Na^+ Cl^-
Cl^- Na^+ Cl^- Na^+ ☐ Na^+

Figure 4.69

(A) Frenkel defect

(B) Frenkel and Schottky defects

(C) Interstitial defect

(D) Schottky defect

Solution

(D) Schottky defect. This is because equal number of cations and anions are missing from their lattice sites.

17. An ionic compound has a unit cell consisting of A ions at the corners of a cube and B ions on the centers of the faces of the cube. The empirical formula for this compound would be **(AIEEE 2005)**

(A) AB (B) A_2B

(C) AB_3 (D) A_3B

Solution

(C) Number of atoms of A = $\frac{1}{8} \times 8$ (corners) = 1

Number of atoms of B = $\frac{1}{2} \times 6$ (faces) = 3

Hence, the formula of compound will be A_1B_3

18. Total volume of atoms present in a face centered cubic unit cell of a metal is (r is atomic radius) **(AIEEE 2006)**

(A) $\frac{20}{3}\pi r^3$ (B) $\frac{24}{3}\pi r^3$

(C) $\frac{12}{3}\pi r^3$ (D) $\frac{16}{3}\pi r^3$

Solution

(D) For a face centered cubic unit cell there are 4 atoms per unit cell.

For one spherical atom volume, $V = \frac{4}{3}\pi r^3$

For 4 atoms volume, $V = \frac{4}{3}\pi r^3 = \frac{16}{3}\pi r^3$

19. In a compound atom of element Y from ccp lattice and those of element X occupy 2/3rd of tetrahedral voids. The formula of the compound will be

(A) X_4Y_3 (B) X_2Y_3

(C) X_2Y (D) X_3Y_4 **(AIEEE 2008)**

Solution

(A) Number of atoms of Y = 4 (as ccp, hence rank = 4)

Number of atoms of $X = \frac{2}{3} \times 8$ (tetrahedral voids are double the rank)

Hence, formula of compound will be X_4Y_3

20. Copper crystallizes in fcc with a unit cell length of 361 pm. What is the radius of copper atom?

(A) 157 pm (B) 181 pm

(C) 108 pm (D) 127 pm **(AIEEE 2009)**

Solution

(D) For fcc, the relationship between edge length (a) and radius of sphere (r) is $(2)^{1/2}\, a = 4r$

$$r = \frac{\sqrt{2}a}{4} = \frac{\sqrt{2} \times 361}{4} = 127 \text{ pm}$$

21. The edge length of a face centered cubic cell of an ionic substance is 508 pm. If the radius of the cation is 110 pm the radius of the anion is

(A) 144 pm (B) 288 pm
(C) 398 pm (D) 618 pm **(AIEEE 2010)**

Solution

(A) For an fcc arrangement,

$$(r^+ + r^-) = \frac{\text{Edge length}}{2} \Rightarrow (110 + r^-) = \frac{508}{2}$$

or $r^- = 144$ pm

22. Percentage of free space in cubic close-packed structure and in body centered packed structure are, respectively,

(A) 48% and 26% (B) 30% and 26%
(C) 26% and 32% (D) 32% and 48%

(AIEEE 2010)

Solution

(C) This is because packing efficiency of cubic close packing and body centered packing are 74% and 68%. So, the free space will be (100 – 74 = 26% and 100 – 68 = 32%).

23. In a face centered cubic lattice, atom A occupies the corner position and atom B occupies the face center positions. If one atom of B is missing from one of the face centered points, the formula of the compound is

(A) AB_2 (B) A_2B_3
(C) A_2B_5 (D) A_2B **(AIEEE 2011)**

Solution

(C) No. of atoms of A (per unit cell) = $1/8 \times 8 = 1$
No. of atoms of B (per unit cell) = $(1/2) \times 5$ (because 1 atom is missing from the face) = 5/2
Formula is $A_1B_{5/2} = A_2B_5$

24. Lithium forms body centered cubic structure. The length of the side of its unit cell is 351 pm. Atomic radius of lithium will be: **(AIEEE 2012)**

(A) 75 pm (B) 300 pm
(C) 240 pm (D) 152 pm

Solution

(D) For a bcc structure, the relationship between a (length of the side of the unit cell) and r (atomic radius) is given as $\sqrt{3}a = 4r$ where a is given as 351 pm. So,

$$r = \sqrt{3} \times \frac{351}{4} = 152 \text{ pm}$$

25. Which of the following exists as covalent crystals in the solid state? **(JEE Main 2013)**

(A) Silicon (B) Sulphur
(C) Phosphorus (D) Iodine

Solution

(A) Silicon (Si) exists as covalent solid, sulphur (S_8) exists as molecular solid, phosphorus (P_4) exists as molecular solid and iodine (I_2) exists as molecular solid.

26. CsCl crystallizes in body centred cubic lattice. If 'a' is its edge length then which of the following expressions is correct? **(JEE Main 2014)**

(A) $r_{Cs^+} + r_{Cl^-} = 3a$

(B) $r_{Cs^+} + r_{Cl^-} = \frac{3a}{2}$

(C) $r_{Cs^+} + r_{Cl^-} = \frac{\sqrt{3}a}{2}$

(D) $r_{Cs^+} + r_{Cl^-} = \sqrt{3}a$

Solution

(C) For body centred cubic lattice of CsCl shown in Fig. 4.70

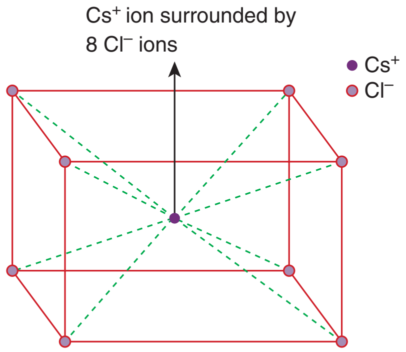


Figure 4.70

Two Cl⁻ and one Cs⁺ touch each other at body diagonal of cube. Thus,

$$2r_{Cs}^{+} + 2r_{Cl}^{-} = \sqrt{3}a \Rightarrow r_{Cs}^{+} + r_{Cl}^{-} = \frac{\sqrt{3}a}{2}$$

REVIEW QUESTIONS

1. What kinds of particles are located at the lattice sites in a metallic crystal?

2. What are crystalline solids? State the categories of crystalline solids with examples.

3. What are the possible types of defects that can occur if a Ca^{2+} ion replaces an Na^+ in an crystal lattice of NaCl?

4. Calculate the packing efficiency of an hcp lattice unit cell.

5. A compound consisting of the monovalent ions A^+, B^- crystallizes in the body centered cubic lattice. **(a)** What is the formula of the compound? **(b)** If one of A^+ ions from the corner is replaced by a monovalent ion C^+, what would be the simplest formula of the resulting compound?

6. What are the similarities and differences between metallic and ionic crystals?

7. Columbium is another name for one of the elements. It is shiny, soft and ductile. It melts at 2468°C, and the solid conducts electricity. What kind of solid does columbium form?

8. Barium metal has body centered cubic structure. Draw a unit cell of barium atom and calculate the number of barium atoms per unit cell.

9. What type of interactions hold the molecules together in a polar molecular solid?

10. Explain the two types of close packing of atoms/ions commonly found in crystalline solids.

11. AgI crystallizes in cubic close-packed ZnS structure. What fraction of tetrahedral sites is occupied by Ag^+ ions?

12. Explain why the presence of Schottky defect in a crystal lowers its density.

13. If the radius of the octahedral void is r and radius of the atoms in close packing is R, derive the relation between r and R.

14. Discuss Schottky and Frenkel defects. Explain with the help of diagrams.

15. Where in the periodic table are the atoms most likely to be involved in the formation of semiconductors located?

16. Figure 4.71 refers to the creation of F-center.

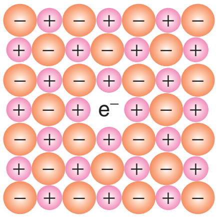


Figure 4.71

(a) What type of solids show this type of defect?
(b) How are F-center formed?

17. Why does germanium act as an n-type semiconductor?

18. The number of vacancies generated in NaCl lattice on addition of divalent ions is twice the number of ions added. Justify.

19. Explain the cause of magnetic behavior in the following type of substance:

(a) Ferromagnetic **(b)** Paramagnetic

20. Distinguish between amorphous and crystalline states of solids. What are the characteristic properties of each type?

21. Indicate which type of crystal (ionic, molecular, covalent, metallic) each of the following would form when it solidifies: **(a)** Br_2, **(b)** LiF, **(c)** MgO, **(d)** Mo, **(e)** Si, **(f)** PH_3, **(g)** NaOH.

22. What relationship is there between a crystal lattice and a unit cell?

23. How many copper atoms are there within the face centered cubic unit cell of copper?

24. What is a tetrahedral void? How many tetrahedral voids can exist per unit cell in a close-packed structure of uniform spheres?

25. What are two ways by which non-stoichiometric defects due to metal deficiency may occur?

26. In chromium (III) chloride, $CrCl_3$, chloride ions have cubic close-packed arrangement and Cr(III) ions are present in the octahedral holes. What fraction of the octahedral holes is occupied? What fraction of the total number of holes is occupied?

27. Name the ions which form the close-packed structure (along with the type of packing) and the ions which fill the voids (along with the types of voids) in the compounds: **(a)** NaCl, **(b)** ZnS, **(c)** CaF_2.

28. To which axis is the (1 1 1) plane parallel to?

29. In the following structure (Fig. 4.72), which voids do the sites S_1 and S_2 represent?

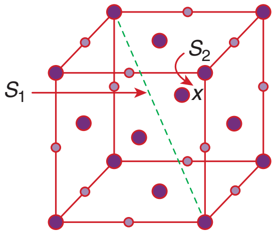


Figure 4.72

30. Which crystal system has no rotation of symmetry?

NUMERICAL PROBLEMS

1. Metallic magnesium has a hexagonal close-packed structure and a density of 1.74 g cm^{-3}. Assuming magnesium atoms to be spherical, calculate the radius of magnesium atom. (Atomic mass of Mg = 24.3 u).

2. Iron changes its crystal structure from body centered to cubic close-packed structure when heated to 916°C. Calculate the ratio of the density of the bcc crystal to that of ccp crystal, assuming that the metallic radius of the atom does not change.

3. Barium crystallizes in a body centered cubic structure in which the cell edge length is 0.5025 nm. Calculate the shortest distance between neighboring barium atoms in the crystal.

4. Chromium metal (ρ = 7.20 g cm^{-3}) crystallizes in a body centered cubic unit cell. Calculate the volume of the unit cell and the radius of a chromium atom.

5. Calcium metal crystallizes in a face centered cubic lattice with edge length of 0.556 nm. Calculate the density of the metal if it contains **(a)** 0.5% Frenkel defects and **(b)** 0.2% Schottky defects.

6. Determine whether calcium crystallizes in a primitive cubic, a body centered cubic, or a face centered cubic unit cell, assuming that the cell edge length is 0.5582 nm and the density of the metal is 1.55 g cm^{-3}.

7. A compound with fcc crystal structure has a density of 2.163×10^3 kg m^{-3}. Calculate the edge length of its unit cell.

8. By X-ray diffraction methods, the unit length of NaCl is observed to be 0.5627 nm. The density of NaCl is found to be 2.164 g cm^{-3}. What type of defect exists in the crystal? Calculate the percentage of Na^+ and Cl^- ions missing.

9. The atomic radius of nickel is 124 pm. Nickel crystallizes in face centered cubic lattice. What is the edge length of the unit cell expressed in pm and Å?

10. For a cubic crystal, the face diagonal is 3.50 Å. Calculate the face length.

11. Lithium borohydride, $LiBH_4$, crystallizes in an orthorhombic system with 4 molecules per unit cell. The unit cell dimensions are: a = 6.81 Å, b = 4.43 Å and c = 7.17 Å. Calculate the density of the crystal. Take atomic mass of Li = 7 u, B = 11 u and H = 1 u.

12. A unit cell of sodium chloride has four formula units. The edge length of the unit cell is 0.564 nm. What is the density of sodium chloride? **[IIT-JEE 1997]**

13. Sodium chloride has face centered cubic (fcc) structure. The density of NaCl is 2.163 g cm^{-3}. Calculate
(a) edge length of cubic cell;
(b) distance between two adjacent atoms.
Given that mass weight of sodium = 23 and mass weight of chlorine = 35.5.

14. The distance between layers of NaCl crystal is 282 pm. X-rays are diffracted from these layers at an angle of 23.0° with first-order diffraction. Calculate the wavelength of X-rays in nm.

15. CuCl has face centered cubic structure. Its density is 3.4 g cm^{-3}. What is the length of unit cell?

16. A compound forms hexagonal close-packed structure. What is the total number of voids in 0.5 mol of it? How many of these are tetrahedral voids?

17. Caesium chloride forms simple cubic lattice in which Cs^+ ions are the corners and Cl^- ion is in the center. The cation–anion contact occurs along the body diagonal of the unit cell. (The body diagonal starts at one corner and then runs through the center of the cell to the opposite corner.).The length of the edge of the unit cell is 412.3 pm. The Cl^- ion has a radius of 181 pm. Calculate the radius of Cs^+ ion.

ADDITIONAL OBJECTIVE QUESTIONS

Single Correct Choice Type

1. Fraction of total volume occupied by atoms in a simple cube is
(A) $\frac{\pi}{2}$ (B) $\frac{\sqrt{3}\pi}{8}$
(C) $\frac{\sqrt{2}\pi}{6}$ (D) $\frac{\pi}{6}$

2. Which of the following is an amorphous solid?
(A) Rubber (B) Plastic
(C) Glass (D) All of these

3. The unit cell of a metallic element of atomic mass 108 and density 10.5 g cm^{-3} is a cube with edge length of 409 pm. The structure of the crystal lattice is
(A) fcc. (B) bcc.
(C) hcp. (D) none of these.

4. Which of the following statements is correct?
(I) The coordination number of cation occupying a tetrahedral hole is 4.
(II) The coordination number of cation occupying a octahedral hole is 6.
(III) In Schottky defects, density of the lattice decreases.
(A) I, II (B) II, III
(C) I, II, III (D) I, III

5. A compound formed by elements A and B crystallizes in a cubic structure where A atoms are at the corners of a cube and B atoms are at the face center. The formula of the compound is
(A) AB_3 (B) AB_2
(C) AB_4 (D) None of these

6. Which arrangement of electrons leads to antiferromagnetism?
(A) ↑↑↑ (B) ↑↓↑↓
(C) Both A and B (D) None of these

7. CsBr has bcc structure with edge length 4.3 Å. The shortest interionic distance in between Cs^+ and Br is
(A) 3.72 Å (B) 1.86 Å
(C) 7.44 Å (D) 4.3 Å

8. When NaCl is doped with $MgCl_2$, the nature of defect produced is
(A) interstitial. (B) Frenkel.
(C) Schottky. (D) None of these.

9. In a cubic packed structure of mixed oxides, the lattice is made up of oxide ions. One-fifth of tetrahedral voids are occupied by divalent (X^{2+}) ions, while one-half of the octahedral voids are occupied by trivalent ions (Y^{3+}), then the formula of the oxide is
(A) XY_2O_4
(B) X_2YO_4
(C) $X_4Y_5O_{10}$
(D) $X_5Y_4O_{10}$

10. The limiting radius ratio of the complex $[Ni(CN)_4]^{2-}$ is
(A) 0.225 – 0.414
(B) 0.414 – 0.732
(C) 0.155 – 0.225
(D) None of these

11. How many tetrahedral holes are occupied in diamond?
(A) 25%
(B) 50%
(C) 75%
(D) 100%

12. A substance A_xB_y crystallizes in a face centered cubic lattice in which atoms A occupy each corner of the cube and atoms B occupy the centers of each face of the cube. Identify the corner composition of the substance A_xB_y.
(A) AB_3
(B) A_4B_3
(C) A_3B
(D) Cannot be determined.

13. A metal crystallizes in two cubic phases, face centered cubic (fcc) and body centered cubic (bcc) whose unit cell length are 3.5 Å and 3.0 Å, respectively. Calculate the ratio of density of fcc and bcc.
(A) 2.123
(B) 1.259
(C) 5.124
(D) 3.134

14. Xenon crystallizes in face centered cubic lattice and edge of the unit cell is 620 pm, then the radius of xenon atom is
(A) 219.20 pm
(B) 438.5 pm
(C) 265.5 pm
(D) 536.94 pm

15. In a face centered cubic arrangement of metallic atoms, what is the relative ratio of the sizes of tetrahedral and octahedral voids?
(A) 0.543
(B) 0.732
(C) 0.414
(D) 0.637

16. Frenkel defect is noticed in
(A) AgBr
(B) ZnS
(C) AgI
(D) all of these.

17. A crystal formula AB_3 has A ions at the cube corners and B ions at the edge centers. The coordination numbers of A and B are, respectively,
(A) 6 and 6
(B) 2 and 6
(C) 6 and 2
(D) 8 and 8

18. A compound of CuCl has face centered cubic structure. Its density is 3.4 cm^{-3}. The length of unit cell is
(A) 5.783 Å
(B) 6.789 Å
(C) 7.783 Å
(D) 8.783 Å

19. If the ratio of coordination numbers P to that of Q be Y:Z, then the formula of the solid is
(A) P_yQ_z
(B) P_zO_y
(C) $P_{1/y}Q_{1/z}$
(D) none of these.

20. The coordination number of a metal crystallizing in a hexagonal close-packed structure is
(A) 12
(B) 4
(C) 8
(D) 6

21. The number of tetrahedral and octahedral voids in hexagonal primitive unit cell are
(A) 8, 4
(B) 2, 1
(C) 12, 6
(D) 6, 12

22. In the fluorite structure (CaF_2),
(A) Ca^{2+} ions are ccp and F^- ions are present in all the tetrahedral voids.
(B) Ca^{2+} ions are ccp and F^- ions are present in all the octahedral voids.
(C) Ca^{2+} ions are ccp and F^- ions are present in all the octahedral voids and half of ions are present in tetrahedral voids.
(D) None of these.

23. The lattice parameters are $a = 5.62$ Å, $b = 7.41$ Å, $c = 9.48$ Å. The three coordinates are mutually perpendicular to each other. The crystal is
(A) tetragonal.
(B) orthorhombic.
(C) monoclinic.
(D) trigonal.

24. In a solid AB having the NaCl structure, A atoms occupy the corners of the cubic unit cell. If all the face centered atoms along one of the axes are removed, then the resultant stoichiometry of the solid is
(A) AB_2
(B) A_2H
(C) A_4B_3
(D) A_3B_4

25. Ice belongs to which of the following structures?
(A) Cubic
(B) Hexagonal
(C) Orthorhombic
(D) Tetragonal

26. A body centered cubic arrangement is shown in Fig. 4.73. O is the body center; A, B, C, D, …, H are the corners. What is the magnitude of the angle AOB?

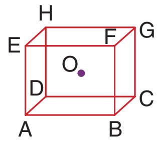


Figure 4.73

(A) 120°
(B) 109° 28′
(C) 104° 31′
(D) 70° 32′

27. A binary solid (A^+B^-) has a zinc blende structure with B^- ions constituting the lattice and A^+ ions occupying 25% tetrahedral holes. The formula of solid is
(A) AB
(B) A_2B
(C) AB_2
(D) AB_4

28. Iron crystallizes in a body centered cubic structure. The radius of Fe atom (if edge length of unit cell is 286 pm) is
(A) 120.9 pm
(B) 123.8 pm
(C) 23.8 pm
(D) 223.8 pm

29. Gold crystallizes in the face centered lattice. The number of unit cells in 1 g of gold (atomic mass = 197 u) will be
(A) 6.02×10^{23}
(B) 7.64×10^{20}
(C) 3.82×10^{20}
(D) 15.28×10^{20}

30. Potassium crystallized in a body centered cubic lattice. What is the approximate number of unit cells in 4.0 g of potassium? (Atomic mass of potassium = 39 u.)

(A) 3.09×10^{22}
(B) 2.09×10^{21}
(C) 4.10×10^{21}
(D) 3.09×10^{20}

31. In a crystal, both ions are missing from normal sites in equal number. This is an example of
(A) F-centers.
(B) interstitial defect.
(C) Frenkel defect.
(D) Schottky defect.

32. When transition metals form interstitial compounds, the non-metals (H, B, C, N) are accommodated in
(A) voids or holes in cubic in cubic-packed structure.
(B) tetrahedral voids.
(C) octahedral voids.
(D) all of these.

33. Among the following types of voids, which one is the largest void?
(A) Triangular system
(B) Tetragonal system
(C) Monoclinic system
(D) Octahedral system

34. The anions A form hexagonal closest packing and atoms C occupy only 2/3 of octahedral voids in it, then the general formula of the compound is
(A) CA
(B) A_2
(C) C_2A_3
(D) C_3A_2

35. A metallic element exists as cubic lattice. Each edge of the unit cell is 241 Å. The density of the metal is $7.20\,g\,cm^{-3}$. How many unit ceil will be present in 100 g of the metal?
(A) 6.85×10^{2}
(B) 5.82×10^{23}
(C) 4.37×10^{5}
(D) 2.12×10^{6}

36. The most efficient packing of similar spheres is obtained in
(A) the simple cubic system and the body centered cubic system.
(B) the simple cubic system and the hexagonal close packed system.
(C) the face centered cubic system and the hexagonal close packed system.
(D) the body centered cubic system and the face centered cubic system.

37. Bragg's equation is
(A) $n\lambda = 2\theta\sin\theta$
(B) $n\lambda = 2d\sin\theta$
(C) $2n\lambda = d\sin\theta$
(D) $\lambda = (2d/n)\sin\theta$

38. A solid PQ has rock salt type structure in which Q atoms are at the corners of the unit cell. If the body centered atoms in all the unit cells are missing, the resulting stoichiometry will be
(A) PQ
(B) PQ_2
(C) P_3Q_4
(D) P_4Q_3

39. Choose the correct matching sequence from the possibilities given

Column I	Column II
(A) Crystal defect	(p) AB AB AB type crystal
(B) hcp	(q) Covalent crystal
(C) CsCl	(r) Frenkel defect
(D) Diamond	(s) Face centered in cube
(E) NaCl	(t) Body centered in cube

	(A)	(B)	(C)	(D)	(E)
(a)	(r)	(p)	(q)	(t)	(s)
(b)	(r)	(p)	(t)	(q)	(s)
(c)	(r)	(t)	(p)	(q)	(s)
(d)	(t)	(p)	(s)	(q)	(p)

Multiple Correct Choice Type

1. Which of the following statement(s) is(are) correct?
(A) The coordination number of each type of ion in CsCl crystal is 8.
(B) A metal that crystallizes in bcc structure has a coordination number of 12.
(C) A unit cell of an ionic crystal shares some of its ions with other unit cells.
(D) The length of the unit cell in NaCl is 552 pm. ($r_{Na^+} = 95$ pm; $r_{Cl^-} = 181$ pm).

2. Which of the following compounds represent a normal 2:3 spinel structure?
(A) $Mg^{II}Al_2^{III}O_4$
(B) $Co^{II}(Co^{III})_2O_4$
(C) $Zn(TiZn)O_4$
(D) $Ni(CO)_4$

3. Pick up the correct statements
(A) The ionic crystal of AgBr has Schottky defect.
(B) The unit cell having crystal parameters, $a = b \neq c$, $\alpha = \beta = 90°, \gamma = 120°$ is hexagonal.
(C) In ionic compounds having Frenkel defect, the ratio r^+/r^- is high.
(D) The coordination number of Na^+ ion in NaCl is 4.

4. Select the correct statements:
(A) The conductance through electrons is called *p*-type conduction.
(B) The conductance through positive holes is called *p*-type conduction.
(C) The conductance through electros holes is called *n*-type conduction.
(D) The band gap in germanium is small.

5. Which of the following are not the characteristics of crystalline solids?
(A) They are isotropic.
(B) They are polymorphism.
(C) After melting, they become non-crystalline.
(D) They do not have thermodynamic defects.

6. The hcp and ccp structure for a given element would be expected to have
(A) the same coordination number.
(B) the same density.
(C) the same packing fraction.
(D) all of these.

7. TiO_2 (rutile) shows 6:3 coordination. Which of the following solids have a rutile-like structure?

(A) MnO_2 (B) ZnS
(C) KCl (D) SnO_2

8. Select the correct statements about three-dimensional hcp system:
(A) The volume atoms in hcp unit cell is six.
(B) The volume of hcp unit cell is $24\sqrt{2}r^3$.
(C) The empty space in hcp unit cell is 26%.
(D) The base are of hcp unit is $6\sqrt{3}r^3$.

9. In the fluorite structure if the radius ratio is $\left(\sqrt{\frac{3}{2}}-1\right)$. How many ions does each cation touch?
(A) 4 anions (B) 12 cations
(C) 8 anions (D) No cations

10. The density of a certain solid AB (formula mass = 119) is 2.75 g cm^{-3}. The edge of the unit cell is 654 pm long. What is/are true about the solid AB?
(A) It has bcc unit cell.
(B) There are four constituents per unit cell.
(C) Unit cell constituted by anions of fcc.
(D) Structure is similar to ZnS.

11. If the radius of Na^+ ion is 95 pm and that of Cl^- ion is 181 pm, then
(A) coordination number of Na^+ is 6.
(B) Structure of NaCl is octahedral.
(C) Radius of the unit cell is 552 pm.
(D) Edge of the unit cell is 276 pm.

12. The correct statement(s) regarding defects in solids is (are)
(A) Frenkel defects are usually favored by a very small difference in the sizes of a cation and anion.
(B) Frenkel defect is a dislocation defect.
(C) Trapping of an electron in the lattice leads to the formation of F-center.
(D) Schottky defects have no effect on the physical properties of solids.

13. In which of the following lattice systems does a primitive unit cells have $a \neq b \neq c$?
(A) Orthorhombic (B) Monoclinic
(C) Triclinic (D) Hexagonal

14. Which of the following statement is correct?
(A) A rutile (TiO_2) structure consists of an hcp anion lattice with cations occupying half the octahedral holes.
(B) The Wurtzite structure is derived from an expanded hcp anion array with cation occupying one type of octahedral holes.
(C) In the fluorite structure (CaF_2), anions occupy both types of tetrahedral holes in an expanded fcc lattice of cations.
(D) None of these.

15. Which of the following is/are true?
(A) In hexagonal close packing, each atom has a coordination number of 6.
(B) In body centered cubic, the space occupied by spheres is 68%.
(C) Solids have either tetrahedral voids or octahedral voids.
(D) There is no difference between fcc and ccp arrangements.

16. The elements of symmetry in a crystal are
(A) plane of symmetry. (B) axis of symmetry.
(C) center of symmetry. (D) none of these.

17. Ferromagnetic substances among the following are
(A) gold. (B) nickel.
(C) silver. (D) gadolinium.

18. Which of the following crystals have 8:8 coordination?
(A) NH_4Cl (B) AlFe
(C) MnO (D) NH_4Br

19. Which of the following is/are false?
(A) $MgFe_2O_4$ is a ferrite but $ZnFe_2O_4$.
(B) Ferrites have spine structure.
(C) The number of tetrahedral voids is four times that of octahedral voids.
(D) If the radius of anion is double than that of cations, the crystalline solid has octahedral structure.

20. If radius of anion is 0.20 nm, the maximum radius of cations which can be filled in respective voids are correctly matched in:
(A) $r^+ = 0.0828$ nm for tetrahedral void
(B) $r^+ = 0.045$ triangular void
(C) $r^+ = 0.1464$ nm for octahedral void
(D) none of these.

21. Choose the correct statements
(A) Vacancy defects lower the density of a substance.
(B) Interstitial defects increase the density of a substance.
(C) Schottky defects preserve the electrical neutrality of a crystal.
(D) Frenkel defects do not affect the density of a crystal.

22. Molecular crystals may exist in
(A) crystalline state. (B) amorphous state.
(C) non-crystalline state. (D) none of these.

23. Which of the following statement are correct for the rock salt structure?
(A) The tetrahedral sites are smaller than octahedral sites.
(B) The octahedral sites are occupied by cations and the tetrahedral sites are empty.
(C) The radius ratio is 0.732.
(D) The radius ratio is 0.999.

24. *p*-type semiconductors are produced when
(A) silicon is doped with boron.
(B) germanium is doped with phosphorus.
(C) germanium is doped with aluminium.
(D) silicon is doped with arsenic.

25. Select the correct statements about solid crystals.
(A) High pressure decreases coordination number.
(B) High pressure increases coordination number
(C) High temperature increases coordination number.
(D) High temperature decreases coordination number.

26. Which of the following possesses rock salt type structure?
(A) KBr (B) CsBr
(C) CaO (D) BeS

27. The space in which atoms are not present in unit cell is(are)
(A) in sc 48% (B) in fcc 26%
(C) in bcc 32% (D) in hexagonal 26%

Assertion–Reasoning Type

Choose the correct option from the following:

(A) Statement 1 is True, Statement 2 is True; Statement 2 is a correct explanation for Statement 1.
(B) Statement 1 is True Statement 2 is True; Statement 2 is NOT a correct explanation for Statement 1.
(C) Statement 1 is True, Statement 2 is False.
(D) Statement 1 is False, Statement 2 is True.

1. **Statement 1:** The number of the nearest neighbors of any constituent particle is called its coordination number.

Statement 2: Coordination number of atoms in a cubic close packed structure is 8.

2. **Statement 1:** A tetrahedral void is formed when one sphere (or particle) is placed in the depression formed by three particles placed in a plane.

Statement 2: The empty space at the center of six spheres placed octahedrally is the octahedral void.

3. **Statement 1:** Due to Frenkel defect, there is no effect on the density of crystalline solid.

Statement 2: In Frenkel defect, no cation or anion leaves the crystal.

4. **Statement 1:** In close packing of spheres, a tetrahedral void is surrounded by four spheres, whereas an octahedral void is surrounded by six spheres.

Statement 2: A tetrahedral void has a tetrahedral shape, whereas an octahedral void has an octahedral shape.

5. **Statement 1:** In hcp, voids are between three touching spheres whose centers lie at the corners of an equilateral triangle.

Statement 2: In hcp, voids are called as square voids.

6. **Statement 1:** The effective number of octahedral voids in ccp structure is 4 per unit cell.

Statement 2: In the ccp structure, there is one octahedral void in the center of the body and 12 octahedral voids on the 12 edges of the cube and each of these edge-based voids is shared by four unit cells.

7. **Statement 1:** Due to the presence of strong coulombic forces between the ions, and close-packed structure, ionic solids are hard.

Statement 2: In ionic solids, the shearing stress is different in different directions.

8. **Statement 1:** In AgCl crystal, Frenkel defect can be observed.

Statement 2: Ag^+ is a small sized atom.

9. **Statement 1:** In hexagonal close packing, the third layer duplicates the first layer.

Statement 2: In hcp, the pattern is ABABAB….

10. **Statement 1:** The melting point decreases in the order: Water > ethyl alcohol > diethylether > methane.

Statement 2: The strength of the intermolecular forces between these molecules follow the order water > ethyl alcohol > diethylether > methane.

11. **Statement 1:** In primitive unit cell, the number of octahedral voids is 1.

Statement 2: The number of octahedral voids in a unit cell containing in it, is equal to the number of atoms the unit cell contains.

12. **Statement 1:** Glass is an amorphous material, whereas quartz is a crystalline substance.

Statement 2: Glass has only short-range order, whereas quartz has a long-range order.

13. **Statement 1:** The 8:8 coordination of CsCl at low temperature changes to 6:6 coordination at 760 K.

Statement 2: Temperature also influences the structure of solid.

14. **Statement 1:** Octahedral holes are present at edge center and at body center in fcc unit cell.

Statement 2: Contribution of holes (octahedral) at edge center is (1/4) and that at body center is 1.

15. **Statement 1:** The stability of a crystal gets reflected in its melting point.

Statement 2: The stability of a crystal depends upon the strength of the interparticle attractive force. The melting point of a solid depends on the strength of the attractive force acting between the constituent particles.

Comprehension Type

Read the paragraphs and answer the questions that follow.

Paragraph I

In a primitive cubic unit cell, all the eight corners of the cube are occupied by the same atoms/ions and not found anywhere else in the cube. The number of atoms within a unit cell is called the rank of a unit cell. For primitive cubic unit cell, the rank (z) is 1. In a bcc, the same atoms/ions are present at all the eight corners of a cube and one atom/ion is also present at the center of the cube. These atoms/ions are not present anywhere else in the cube. The rank of a bcc is 2. In an fcc, the same atoms/ions are present at all the corners of the cube and are also present at the center of each square face. These atoms/ions are not present anywhere else in the unit cell. The rank of an fcc is 4.

1. How many unit cells are present in 39 g of potassium that crystallizes in bcc structure (atomic mass of K = 39 u)?
(A) 0.5 N_A (B) 0.25 N_A
(C) N_A (D) 0.75 N_A
where N_A means Avogadro's constant.

2. Li crystallizes in bcc. The edge length of unit cell is 351 pm. What would be radius of Li atom?
(A) 151.98 pm
(B) 273 pm
(C) 290 pm
(D) 76 pm

3. Sodium crystallizes in bcc lattice. If the length of the edge of the unit cell is 424 pm, density of sodium is (atomic mass of sodium = 23 u)
(A) 10.4 g cm^{-3}
(B) 1.002 g cm^{-3}
(C) 50.4 g cm^{-3}
(D) none of these

Paragraph II

Solids have an ordered arrangement of atoms, but they do not possess a perfect structure. There imperfections or defects in their structure are of different types – point defects and line defects. Point defects are of three types – stoichiometric defects, impurity defects and non-stoichiometric defects.

The two types of stoichiometric defects are vacancy defects and interstitial defects. In ionic solids, these defects are present as Frenkel and Schottky defects.

Non-stoichiometric defects are of metal excess type and metal deficient type. Some solids are difficult to prepare in the stoichiometric composition, for example, pure FeO is difficult to obtain and normally we get a composition of $Fe_{0.95}O$ but it may range from $Fe_{0.93}O$ to $Fe_{0.96}O$. ZnO is normally a white, finely divided material with the Wurtzite structure. On heating, the color changes to yellow due to the evaporation of oxygen from the lattice to give a non-stoichiometric phase. This produces lattice defects which trap electrons that can subsequently be excited by absorption of visible light. Defects are introduced in ionic solids by adding ions having different charge from that of constituting ions.

Impurity defects occur when a molten metal containing impurities is crystallized, the impurity occupies the sites of the metal. In ionic solids, when the ionic impurity has a different valence than the main compound, some vacancies are created. Sometimes calculated amounts of impurities are introduced by doping in semiconductors that change their electrical properties. These are widely used in electronics industry. Solids show magnetic properties such as paramagnetism, diamagnetism, ferromagnetism, antiferromagnetism and ferrimagnetism.

4. In the presence of Frenkel defects in a crystal, the density of the crystal
(A) decreases.
(B) increases.
(C) does not change.
(D) increases or decreases depends on material.

5. Yellow form of ZnO shows enhanced electrical conductivity due to
(A) the elections trapped in neighborhood of excess metal accommodated interstitially.
(B) an excess of O^{2-} ions.
(C) an excess of metal ions accommodated interstitially.
(D) high temperature.

6. When a Group 13 element is added in small amounts to germanium, we get
(A) *n*-type semiconductors.
(B) *p*-type semiconductors.
(C) insulators.
(D) rectifiers.

7. $Fe_{0.95}O$ can be due to presence of iron in +2 and +3 oxidation numbers. Then iron present in +3 oxidation state will be
(A) 15%
(B) 13.5%
(C) 10.5 %
(D) 8.85%

8. An atom containing an odd number of electrons is
(A) paramagnetic.
(B) diamagnetic.
(C) ferromagnetic.
(D) antiferromagnetic.

9. If AgCl is doped with 10^{-4} mol% of $CdCl_2$, then the concentration of cation vacancies per mol will be
(A) 6.02×10^{16}
(B) 6.02×10^{17}
(C) 6.02×10^{18}
(D) 6.02×10^{14}

Paragraph III

Density of a unit cell is the same as the density of the substance. So, if the density of the substance is known, we can calculate the number of atoms or dimensions of the unit cell. The density of the unit cell is related to its mass (M), number of atoms per unit cell (z), edge length (a in cm), and Avogadro's constant N_A as:

$$\rho = \frac{z \times M}{a^3 \times N_A}$$

10. An element X crystallizes in a structure having an fcc unit cell of an edge 100 pm. If 24 g of the element contains 24×10^{23} atoms, the density is
(A) 2.40 g cm^{-3}
(B) 40 g cm^{-3}
(C) 4 g cm^{-3}
(D) 24 g cm^{-3}

11. The number of atoms present in 100 g of a bcc crystal (density = 12.5 g cm^{-3}) having cell edge 200 pm is
(A) 1×10^{25}
(B) 1×10^{24}
(C) 2×10^{24}
(D) 2×10^{26}

12. A metal A (atomic mass = 60 u) has a body centered cubic crystal structure. The density of the metal is 4.2 g cm^{-3}. The volume of unit cell is
(A) 8.2×10^{-23} cm^3
(B) 4.74×10^{-23} cm^3
(C) 3.86×10^{-23} cm^3
(D) None of these.

Integer Answer Type

The answer is a **non-negative integer**.

1. In hexagonal primitive unit cell, the corner is shared by ________ atoms.

2. How many octahedral voids are present per unit cell in an fcc arrangement of particles?

3. What will be the coordination number of Ca^{2+} ion in a fluorite crystal?

4. How many molecules of NaCl are there in an unit cell of its crystal?

5. Iron(II) oxide has a cubic structure and each unit cell has side 500 pm. If the density of the oxide is 4 g cm^{-3}, the number of oxide ions present in each unit cell is ________. (Molar mass of FeO = 72 g mol^{-1}, $N_A = 6.02 \times 10^{23}$ mol^{-1}.)

6. A atoms construct fcc type structure in which B atoms occupy all the octahedral voids. If all the atoms are removed from one of the face of unit cell, then the new empirical formula is A_xB_y. The value of $(x + y)$ is ________.

7. The rank of atoms in the hexagonal unit cell is ________.

8. The radius of Ag^+ ion is 126 pm whereas that of I^- ion is 216 pm. The coordination number of Ag in AgI is ________.

Matrix–Match Type

1. Match the crystals with their structural characteristics.

Column I	Column II
(A) ZnS crystal	(p) fcc
(B) CaF_2 crystal	(q) hcp
(C) NaCl crystal	(r) Distance between closest particles is $(\sqrt{3/4})a$
(D) Diamond crystal	(s) Only one type of voids are occupied

2. Match the structure/compound with the percentage of tetrahedral and octahedral voids.

Column I	Column II
(A) Normal spinel structure	(p) 50% tetrahedral and 100% octahedral voids are unoccupied
(B) Inverse spinel structure	(q) 87.5% tetrahedral and 50% octahedral voids are occupied
(C) Diamond	(r) 100% tetrahedral void are occupied
(D) Na_2O	(s) 50% octahedral and 87.5% tetrahedral voids are unoccupied

3. Match the imperfection in solids with the characteristic features.

Column I	Column II
(A) Schottky defects	(p) Excess cations occupy interstitial sites
(B) Frenkel defects	(q) Conduct electricity due to free electrons
(C) Metal excess defects	(r) Form *p*-type semiconductors
(D) Metal deficient defects	(s) Are non-stoichiometric defects

4. Match the unit cells with their characteristics.

Column I	Column II
(A) sc	(p) $z = 4;\ r = \dfrac{a}{2\sqrt{2}}$
(B) bcc	(q) $z = 2;\ r = \dfrac{\sqrt{3}a}{4}$
(C) fcc	(r) $z = 1;\ r = \dfrac{a}{2}$
(D) hcp	(s) $z = 6;\ r = \dfrac{a}{2}$

ANSWERS

Review Questions

1. Metal cations

3. Impurity defects

5. **(a)** AB; **(b)** A_7BC_8

9. Dipole–dipole interactions

13. $r = 0.414\ R$

16. **(a)** Ionic solids and alkali halides

23. Four atoms

26. 1/3; 1/9

29. S_1 – tetrahedral void, S_2 – octahedral void

2. Categories are metallic solids, ionic solids, covalent solids and molecular solids

4. 74%

7. Metallic solid

11. Half

15. Ceramics

21. **(a, f)** Molecular; **(b, c, g)** ionic; **(d)** metallic; **(e)** covalent

24. Eight

28. *x*, *y* and *z* axes

30. Triclinic

Numerical Problems

1. 1.6×10^{-8} cm

3. 4.352×10^{-8} cm

5. **(a)** $1.5458\ g\ cm^{-3}$; **(b)** $1.5427\ g\ cm^{-3}$

2. 0.919

4. 1.25×10^{-8} cm

6. fcc

7. 563.4 pm.
8. Schottky defect; 0.8%
9. 352 pm or 3.52 Å
10. 2.475 Å
11. 0.676 g cm^{-3}
12. 2.16 g cm^{-3}
13. **(a)** 5.667×10^{-8} cm; **(b)** 1.001×10^{-8} cm
14. 0.477 nm
15. 5.783 Å
16. 9.033×10^{23}; 6.022×10^{23}
17. 176 pm

Additional Objective Questions

Single Correct Choice Type

1. (D) **2.** (D) **3.** (A) **4.** (C) **5.** (A)
6. (B) **7.** (A) **8.** (C) **9.** (C) **10.** (B)
11. (B) **12.** (A) **13.** (B) **14.** (A) **15.** (A)
16. (D) **17.** (C) **18.** (A) **19.** (B) **20.** (A)
21. (C) **22.** (A) **23.** (B) **24.** (D) **25.** (D)
26. (D) **27.** (C) **28.** (B) **29.** (B) **30.** (A)
31. (D) **32.** (D) **33.** (D) **34.** (C) **35.** (B)
36. (C) **37.** (B) **38.** (C) **39.** (B)

Multiple Correct Choice Type

1. (A, C, D) **2.** (A, B) **3.** (B, C) **4.** (B, C, D) **5.** (A, D)
6. (A, C) **7.** (A, D) **8.** (A, B, C, D) **9.** (B, C) **10.** (B, C)
11. (A, B, C) **12.** (B, C) **13.** (A, B, C) **14.** (A, B, C) **15.** (B, D)
16. (A, B, C) **17.** (B, D) **18.** (A, B, D) **19.** (A, C) **20.** (A, B, C)
21. (A, B, C, D) **22.** (A, B, C) **23.** (A, C) **24.** (A, C) **25.** (B, D)
26. (A, C) **27.** (A, B, C, D)

Assertion–Reasoning Type

1. (C) **2.** (B) **3.** (A) **4.** (B) **5.** (C)
6. (A) **7.** (B) **8.** (A) **9.** (A) **10.** (A)
11. (D) **12.** (B) **13.** (A) **14.** (A) **15.** (A)

Comprehension Type

1. (A) **2.** (C) **3.** (A) **4.** (C) **5.** (A)
6. (B) **7.** (C) **8.** (A) **9.** (B) **10.** (B)
11. (C) **12.** (B)

Integer Answer Type

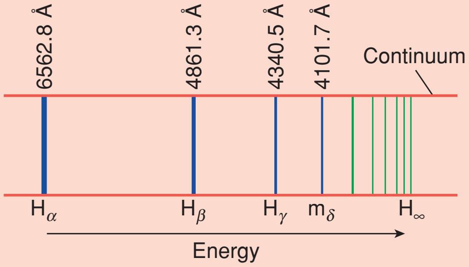
1. (6) **2.** (4) **3.** (8) **4.** (4) **5.** (4)
6. (6) **7.** (6) **8.** (6)

Matrix–Match Type

1. A → (p, q, r, s); B → (p, r, s), C → (p, s), D → (p, r, s)
2. A → (q); B → (s), C → (p), D → (r)
3. A → (q); B → (p, q), C → (p, q, s), D → (r, s)
4. A → (r); B → (q), C → (p), D → (s)

5

Atomic Structure



Spectrum of hydrogen in the visible region

The concept of the atom – a particle so small that until recently it could not be seen even with the most powerful microscope – and the subsequent determination of its structure stand among the greatest creative intellectual human achievements. A fundamental question concerned the fact that classical physics predicted that atoms simply could not exist.

The earliest theories about atoms imagined them to be indestructible and totally unable to be broken into smaller pieces. The diameter of a single atom ranges from 0.1 to 0.5 nm (1 nm = 1×10^{-9} m). Dalton's theory offered logical explanation of many experimental observations and laws that were known at the time, such as – the law of conservation of mass, law of constant composition and law of multiple proportion. It, however, failed to explain certain observations about properties of materials, such as the ability of glass or ebonite rod to generate electricity when rubbed with silk or fur. Now we know that, atoms are not quite as indestructible as Dalton had postulated. During the late 1800s and early 1900s, experiments were performed which demonstrated that atoms are composed of subatomic particles. Many subatomic particles were discovered in the 20th century; however, we will study about electrons, protons and neutrons in detail.

Emerging studies of particles, such as electrons, passing through very small openings gave results (diffraction patterns) that could only be explained if we regarded particles as waves. This led to the concept of the **wave–particle duality** of matter and energy. The above problems with classical physics made it clear that an entirely new set of concepts would be needed to define modern physics and chemistry. These concepts are commonly called **wave mechanics**, **quantum mechanics**, or **quantum theory** and they are now a cornerstone of modern chemistry. This chapter begins with experiments leading to understanding of atom and the subatomic particles.

Contents

5.1 Discovery of Electron
5.2 Discovery of Protons and Neutrons
5.3 Some Prerequisites of Physics
5.4 Atomic Models
5.5 Representation of Atom with Electrons and Neutrons
5.6 Nature of Waves
5.7 Nature of Electromagnetic Radiation
5.8 Planck's Quantum Theory
5.9 Spectra – Continuous and Discontinuous Spectrum
5.10 Bohr's Model for Hydrogen Atom
5.11 Photoelectric Effect
5.12 Dual Nature of Matter
5.13 Heisenberg's Uncertainty Principle
5.14 Number of Waves Made by the Electron
5.15 Quantum Mechanical Model of Atom
5.16 Radial and Angular Wave Functions
5.17 Orbitals and Quantum Numbers
5.18 Electronic Configuration of Atoms
5.19 Magnetic Properties

It further describes the electronic configurations and relates these to the differences in the physical and chemical properties of elements and in the nature of compounds formed by them.

Light emitted from atoms gives us clues about how electrons are arranged within an atom. At the same time an understanding of standing waves develops insights to explain why atoms do not collapse. Therefore, this chapter introduces quantum mechanics by describing the nature of electromagnetic radiation.

5.1 | DISCOVERY OF ELECTRON

In the later part of the nineteenth century, scientists began to experiment with glass tubes in which a high-voltage electric current was passed through a gas at low pressure. Under ordinary conditions, gases are poor conductors of electricity, however when a high voltage is applied to them at low pressure, the gases behave as conductors and current flows through them in the form of rays, which interact with the glass tube and cause the glass tube to glow. This flow of electricity is called an electric discharge, and so the tube is called discharge tube. The existence of these rays was studied first by William Crookes in 1879 using discharge tube, which is a long glass tube, sealed at both the ends and fitted with two metal electrodes. It is also known as **Crookes tube**. The tubes are connected to a vacuum pump which is used to reduce the pressure of gas in the tube.

Note: The electrical discharge could be observed only at very low pressures and high voltage. The pressure could be adjusted for the gases by evacuation.

Tests soon revealed that these rays were, in fact, negatively charged particles moving from the negative electrode (the cathode) to the positive electrode (the anode). It was Benjamin Franklin who decided which electrode was positive and which was negative. These rays were called emissions rays, and because the rays came from the cathode, they were called **cathode rays**. If a hole is made in the anode, the flow of the current from cathode to anode may be checked. If the tube behind the anode is coated with zinc sulphide, then a bright spot on the coating is developed (Fig. 5.1).

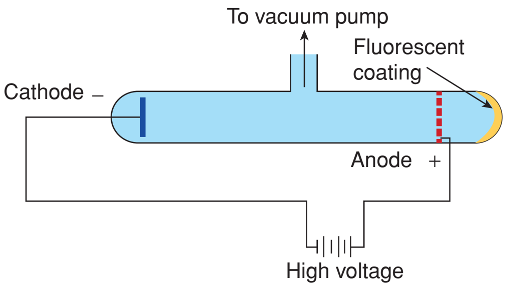


Figure 5.1 A perforated anode in a cathode ray discharge tube.

Thomson Experiment – Determination of Mass to Charge Ratio

In 1897, the British physicist J.J. Thomson constructed a special *cathode ray tube* to make quantitative measurements [the ratio of electrical charge (e) to the mass of electron (m_e)] of the properties of cathode rays. In some ways, the cathode ray tube he used was similar to a TV picture tube, as shown in Fig. 5.2. In Thomson's tube, a beam of cathode rays was focused on a glass surface coated with a phosphor; this surface glows when the cathode rays strike on it. The results of these experiments established the following properties of cathode rays:

1. These cathode rays flow from cathode to anode in *straight line*, unless influenced by electrical or magnetic fields.
2. These rays are not visible as such and can be detected by fluorescent or phosphorescent materials which glow when these rays fall on them.
3. That cathode rays are negatively charged. This can be proved since they behave like negatively charged particles under the influence of electric and magnetic fields.
4. The experiments performed using the cathode ray tube demonstrated that cathode ray particles are in all matter. They are, in fact, **electrons**. The properties of electrons are independent of electrode material and nature of the gas.
5. Cathode rays are made up of material particles and this was demonstrated by the fact that they could rotate the light paddlewheel mounted on an axle.
6. When the cathode rays strike the metal foil, it becomes heated, showing that cathode rays produce heating effect.
7. They show penetrating effect and ionize the gas through which they pass. This property is exploited in making television sets containing cathode ray tubes.

The cathode ray beam passed between the poles of a magnet and between a pair of metal electrodes that could be given electrical charges. When electrical or magnetic fields are applied perpendicular to the path of charged particles, they deviate from their path and the amount of deviation depends on:

1. The magnitude of charge on the particle. Greater the magnitude of charge, greater is the interaction with the field, and hence higher is the deviation.
2. The mass of the charged particle. Heavier particles are deviated to a lesser extent.
3. The strength of the magnetic field or the voltage applied across the path of the charged particles.

The magnetic field tends to bend the beam in one direction (see property 2) whereas the charged electrodes bend the beam in the opposite direction (see property 3). By adjusting the charge on the electrodes, the two effects can be made to cancel, and from the amount of charge on the electrodes required to balance the effect of the magnetic field, Thomson was able to calculate the first bit of quantitative information about a cathode ray particle – the ratio of its charge to its mass as 1.758820×10^{11} C kg^{-1}, where the coulomb (C) is a standard unit of electrical charge. The particles are negatively charged so the charge on the electron is $-e$. Therefore,

$$\frac{e}{m_e} = 1.758820 \times 10^{11} \text{ C kg}^{-1}$$

where m_e is the mass of the electron.

Note: Heating effect $\propto m$ and penetrating effect $\propto \frac{1}{m}$.

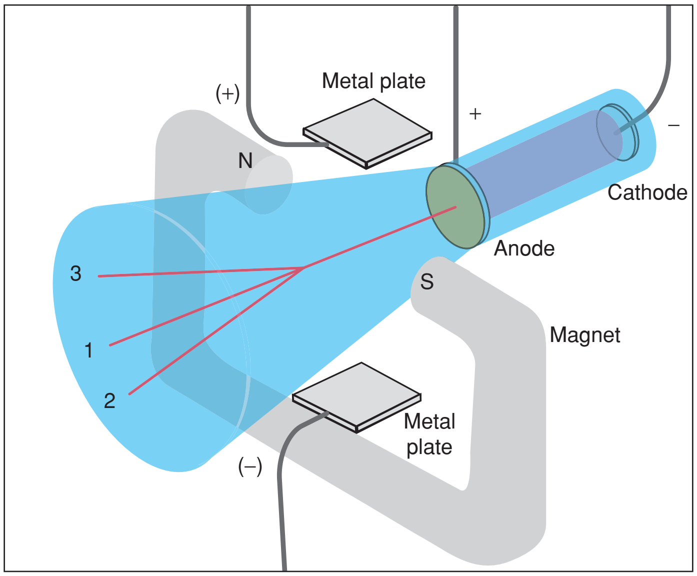


Figure 5.2 Thomson's cathode ray tube.

Millikan Oil Drop Experiment – Charge on an Electron

In 1909, Robert Millikan, a researcher at the University of Chicago, designed an experiment in which he sprayed a fine mist of oil droplets above a pair of parallel metal plates, the top one of which had a small hole in it. As the oil drops settled, some passed through this hole into the space between the plates, where he irradiated them briefly with X-rays. The X-rays knocked off electrons from molecules in the air, and the electrons attached to the oil drops, which thereby were given an electrical charge. By observing the rate of fall of the charged drops, both when the metal plates were electrically charged and when they were not, Millikan was able to calculate the amount of charge carried by each drop. When he examined his results, he found that all the values he obtained were whole number multiples of -1.60×10^{-19} C. He reasoned that since a drop could only pick up whole numbers of electrons, this value must be the charge carried by each individual electron. This concept is called quantization of charge, according to which charge of any particle can be expressed as integral multiple of electronic charge (e). Thus,

$$q = n\,(e)$$

where $n = \ldots -3, -2, -1, 0, 1, 2, 3 \ldots$ and $e = 1.6 \times 10^{-19}$ C.

Presently, the accepted value of charge is -1.6022×10^{-19} C. Once Millikan had measured the electron's charge, its mass could then be calculated from Thomson's charge-to-mass ratio. This mass was calculated to be 9.09×10^{-28} g. More precise measurements have since been made, and the mass of the electron is currently reported to be 9.109410×10^{-31} kg.

5.2 | DISCOVERY OF PROTONS AND NEUTRONS

Protons were first observed by Goldstein but their nature was discovered by Thomson. To study these, a modification was made in the construction of the cathode ray tube to produce a new device called a *mass spectrometer*. This apparatus was used to measure the charge-to-mass ratios of positive ions. (The removal of electrons from an atom gives a positively charged particle called an **ion**). These ratios were found to vary, depending on the chemical nature of the gas in the discharge tube, showing that their masses also varied. The positively charged particles are different from electrons. The relative charge of a proton is equal in magnitude to that of an electron but opposite in sign (+1). Their charge-to-mass ratio depends on the nature of the gas from which they originate. They may also carry multiple fundamental units of electrical charge. Their pattern of behavior is opposite to that observed in electrons. The lightest positive particle observed was produced when hydrogen was in the tube, and its mass was about 1837 times as heavy as an electron. The actual mass of proton is 1.674×10^{-24} g. The mass of a proton is only very slightly less than that of a hydrogen atom. When other gases were used, their masses always seemed to be whole-number multiples of the mass observed for hydrogen atoms. This suggested the possibility that clusters of the positively charged particles made from hydrogen atoms made up the positively charged particles of other gases. The hydrogen atom, minus an electron, thus seemed to be a fundamental particle in all matter and was named the **proton**, after the Greek word *proteios*, meaning "of first importance" and was characterized in 1919.

The estimation of mass of an atom based on the number protons, however, fell short of the actual mass of the atom and could account for only about half of the mass of the atom. This led to the suggestion for presence of another particle in the nucleus with mass close to or equal to that of proton, but was electrically neutral. The identity of these particles was established by British physicist, James Chadwick in 1932, based on some experimental observations of German physicists Walther Bothe and Herbert Becker in 1930. They noticed that when α-rays were beamed at beryllium, it emitted a neutral radiation that could penetrate 200 mm of lead. They assumed that this neutral radiation was from high-energy γ-rays. Chadwick suggested that the radiation could not be γ-rays and argued that to eject protons at such a high velocity, the rays must have energy higher than that of α-particles. He called these particles neutrons and proved his hypothesis by the following experiment.

$${}^{4}_{2}\text{He} + {}^{7}_{4}\text{Be} \rightarrow {}^{12}_{6}\text{C} + {}^{1}_{0}\text{n}$$

He put a piece of beryllium in a vacuum chamber with some polonium. When the α-rays emitted by polonium struck beryllium, the neutral radiations were emitted. To establish their identity, he put a target in their path and when the rays hit the target, the atoms were knocked out. The atoms became electrically charged in the collision and were caught in a chamber filled with gas that acted as the detector. The number of atoms and their speed was estimated based on the current generated by the gas particles in the chamber, which are ionized by collision with the charged atoms. The mass of neutron was determined as 1.675×10^{-24}, that is nearly equal to that of proton.

The important properties of fundamental particles are given in Table 5.1.

Table 5.1 Properties of select particles

Particle	Electric charge (C)	Mass	
		Kilograms (kg)	Atomic mass units (u)
Electron	-1.60×10^{-19}	$9.109\,382 \times 10^{-31}$	5.485799×10^{4}
Proton	$+1.60 \times 10^{19}$	$1.672\,622 \times 10^{-27}$	1.007276
Neutron	0	$1.674\,927 \times 10^{-27}$	1.008665
Hydrogen atom	0	$1.673\,534 \times 10^{-27}$	1.007825

In an atom, the negatively charged electrons are attracted to positively charged protons. In fact, it is this attraction that holds the electrons around the nucleus. Neutrons have no charge and are said to be electrically neutral (hence the name **neutron**). Because of their identical charges, electrons repel each other. The repulsions between the electrons keep them spread out throughout the volume of the atom, and it is the *balance* between the attractions the electrons feel towards the nucleus and the repulsions they feel towards each other that controls the sizes of atoms. Protons also repel each other, but they are able to stay together in the small volume of the nucleus because their repulsions are apparently offset by powerful nuclear forces that involve other subatomic particles.

Anode Ray Experiment

Since, penetrating power $\propto 1/m$, therefore, the positive ions being heavier than electrons were not able to penetrate the cathode. In the ionization of gas, positive ions and electrons were formed. For example, $\text{He} \rightarrow \text{He}^{2+} + 2e^-$. Electrons were detected in cathode rays but positive ions were not as they could not penetrate the cathode. Thus, a new experimental set-up consisting of the perforated cathode was done and the positive ions were now detected on the cathode side of the discharge tube (Fig. 5.3). Theses rays were known as anode rays. They consisted of the positive ions moving with much smaller speeds relative to electrons and were deflected by application of electric and magnetic fields.

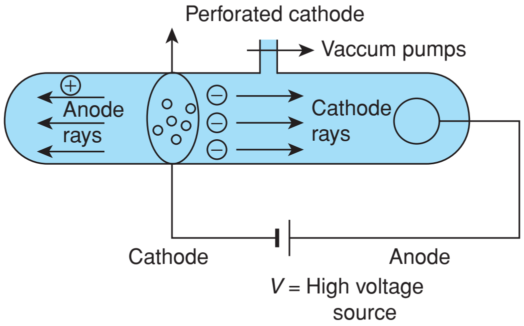


Figure 5.3 Anode ray experiment.

Note: Anode rays consist of the positive ions, not protons directly.

The discussion of atomic structure that follows is based on the assumption that atoms contain only these principal subatomic particles. Nearly all the ordinary chemical properties of matter can be explained in terms of atoms consisting of electrons, protons and neutrons.

Note: The research on subatomic particles over the years has shown that protons and neutrons are themselves composed of still smaller particles called **quarks**. The existence of quarks has led us to understand how the atomic nucleus stays together in spite of the presence of positively charged particles in close proximity. Quarks are, however, unstable outside the confines of the nucleus. Many other subatomic particles, such as mesons, positrons, neutrinos and antiprotons have been discovered, but it is not yet clear whether all these particles are actually present in the atom or whether they are produced by reactions occurring within the nucleus. The fields of atomic and high-energy physics have produced a long list of subatomic particles.

5.3 | SOME PREREQUISITES OF PHYSICS

Some important and useful relations among physical quantities relevant to atomic structure are listed as follows:

1. Force between two charged particles

$$|\vec{F}| = k\frac{q_1q_2}{r^2}$$

where q_1 and q_2 are the charges on the particles and r is the distance between them.

2. Potential energy

$$\text{P.E.} = k\frac{q_1 q_2}{r}$$

3. Electrostatic force

$$|\vec{F}_e| = qE$$

where q is the charge on the particle and E is the electric field acting on the charged particle.

4. Magnetic force

$$|\vec{F}_b| = qvB$$

where q is the charge on the particle moving with velocity v and B is the magnetic field acting on the charged particle, assuming $\vec{v}$ and $\vec{B}$ are perpendicular to each other.

5. Angular momentum

$$|\vec{L}| = mvr$$

where m is the mass of the particle moving with the velocity v in a circular path of radius r.

6. Centripetal acceleration of a particle moving in a circular path of radius r with velocity v.

$$|\vec{a}| = \frac{v^2}{r}$$

5.4 | ATOMIC MODELS

Scientists such as Thomson, Rutherford, Becquerel, Curie and Roentgen and others have contributed to the current model of the atom and explained the distribution of charged particles within the atom. Two of these models proposed by Thomson and Rutherford are discussed as follows.

Thomson Model of Atom

In 1898, Thomson proposed a model of the atom in which, the electrons are negatively charged particles embedded in the atomic sphere of approximate radius 10^{-10} m (Fig. 5.4). Since atoms are electrically neutral, the sphere also contains an equal number of positive charges. The positive charge was assumed to be spread throughout the atom, forming a kind of pudding in which the negative electrons were suspended like plums, hence the name plum pudding model. The mass of the atom is thus assumed to be distributed uniformly over the atom.

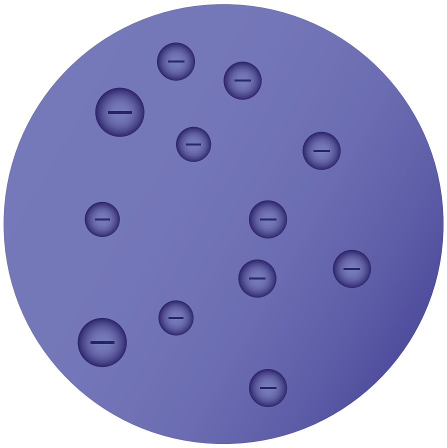


Figure 5.4 Thomson model of the atom.

Note: The model is also known watermelon model because an atom could be visualized as a watermelon of positive charge with electrons as seeds embedded in it.

Drawback: The model proposed by Thomson could explain the neutrality of an atom, but could not account for results for later experiments by Rutherford about distribution of mass.

Rutherford's Nuclear Model of Atom

To understand Rutherford's nuclear model of atom, let us first understand the nature of particles emitted by **radioactive elements**. These elements were found to emit three types of particles, α particles, β particles and γ-rays.

1. An **α particle** is a relatively slow-moving decay product consisting of two protons and two neutrons. It has the lowest penetration power.
2. A **β particle** is a fast-moving electron that is ejected from an unstable nucleus. The electron is produced when a neutron transforms into a proton and electron.

3. A **γ-ray** is the packet of electromagnetic energy released when a nucleus remains unstable after α or β-decay. γ-rays travel at the speed of light and carry no charge. This has the highest penetration power.

At the turn of the 20th century, Ernest Rutherford became interested in the α particles emitted by uranium metal and its compounds. Rutherford found that α particles were absorbed by a thin sheet of metal, but they could pass through metal foil if it was thin enough.

Rutherford noticed that a narrow beam of α particles was broadened as it passed through the metal foil. Working with his assistant Hans Geiger, Rutherford measured the angle through which the α particles were scattered by a thin piece of metal foil. He used a gold foil because gold being unusually ductile can be made into a foil that is only 0.00004 cm (or about 2000 atoms) thick. The thin gold foil had a circular fluorescent zinc sulphide screen around it which emitted light flash whenever α particles struck the screen. When the foil was bombarded with α particles, the α particle had a considerable mass (for a subatomic particle) and it moved quite rapidly.

Based on the Thomson's model of the atom, Rutherford expected the α particles to pass straight through the foil, since electrons with small mass could not deflect them and the positive charge was spread uniformly in the atom. Rutherford and Geiger found that for most of the particles, the angle of scattering was small of the order of 1°. These results were consistent with Rutherford's expectations. However, further investigations by Marsden found that not all particles pass straight through the foil. Some of them are deflected at small angles and a small fraction (perhaps 1 in 20,000) of the α particles were scattered through angles larger than 90° (nearly 180°), that is, they retraced their path [Fig. 5.5(*a*)].

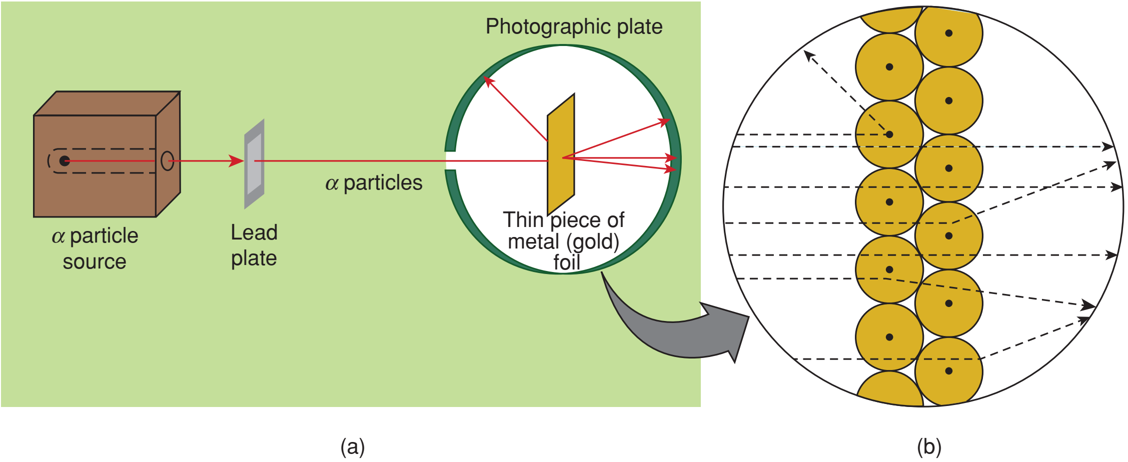


Figure 5.5 (a) A block diagram of the Rutherford–Marsden–Geiger experiment. (b) Passage of particles through the nucleus.

Rutherford found that he could explain Marsden's results by assuming that **the positive charge and most of the mass of an atom are concentrated in a small fraction of the total volume, which he called the nucleus**. Based on this, he explained the experimental observations as follows:

1. Most of the α particles were able to pass through the gold foil without encountering anything large enough to significantly deflect their path.
2. A small fraction of the α particles came close to the nucleus of a gold atom as they passed through the foil. When this happened, the force of repulsion between the positively charged α particle and the nucleus deflected the α particle by a small angle, as shown in Fig. 5.5(b).
3. Occasionally, an α particle travelled along a path that would eventually lead to a direct collision with the nucleus of one of the 2000 or so atoms it had to pass through. When this happened, repulsion between the nucleus and the α particle deflected the α particle through an angle of 90° or more.
4. Rutherford was able to estimate the size of the nucleus and according to his calculations, the radius of the nucleus is at least 10,000 times smaller than the radius of the atom. If the radius of the atom is about 10^{-10} m, then the radius of the nucleus is 10^{-14} m.

$$R = R_o(A)^{\frac{1}{3}}$$

where R is the radius of the nucleus, $R_o = 1.33 \times 10^{-5}$ and A is the mass of the atom.

Note: Consider that an α particle of mass m moves towards the nucleus with velocity v at any given time as shown is Fig. 5.6.

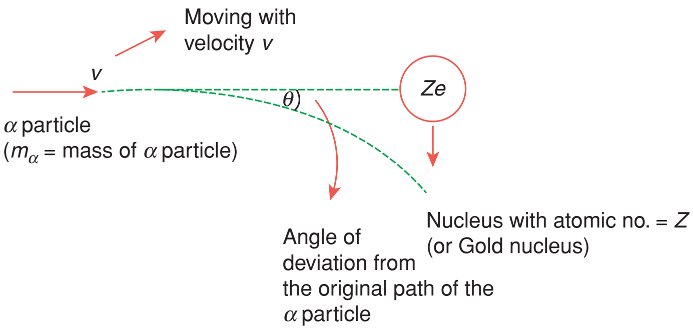

Moving with velocity v
v
Ze
θ)
α particle (m_α = mass of α particle)
Nucleus with atomic no. = Z (or Gold nucleus)
Angle of deviation from the original path of the α particle

Figure 5.6 Alpha particle moving towards nucleus with velocity v.

$N(\theta)$ = Number of α particles with deviation θ. For example, $N(45)$ = number of α particles with deviation 45°. Now, since θ is the deviation, we have

$$0 \le \theta \le 180° \qquad \text{(as maximum deviation = 180°)}$$

$$0 \le \frac{\theta}{2} \le 90°$$

It is observed that

$$N(\theta) \propto \frac{1}{\sin^4(\theta/2)}.$$

Therefore, as θ increases, $\theta/2$ increases and, $N(\theta)$ decreases.

Hence, $N(0)$ is maximum, that is, number of particles with no deviations is maximum. In other words, most of the α particles passed through the gold foil without any deviation.

$N(180)$ is minimum, that is, number of particles with 180° deviation is minimum. In other words, very few α particles were deflected by 180°.

Impact Parameter (b)

To find the impact parameter, draw a line of motion of the α particles by extending its path in the direction of velocity. Then draw a parallel line to this line of motion passing through the center of the nucleus (Fig. 5.7). The shortest distance between two lines is known as the impact parameter (b).

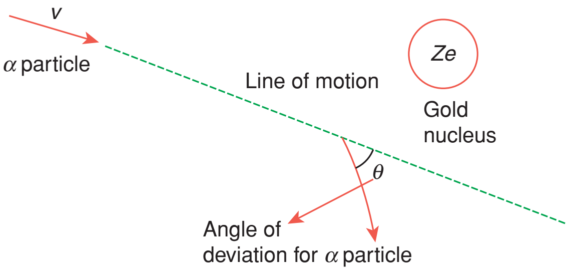


Figure 5.7 Determining impact factor.

It is observed that

$$b \propto \frac{1}{\tan^2\left(\frac{\theta}{2}\right)}$$

$$0 \le \theta \le 180°$$

$$0 \le \frac{\theta}{2} \le 90°$$

As θ increases, $\theta/2$ increases and b decreases. As b decreases or distance of α particles to the center of the gold nucleus decreases, its deviation increases. This means that α particles which are close to the nucleus are bound to deflect more than α particles which are farther from the nucleus.

Distance of Closest Approach

When the α particles move towards the nucleus at a certain point its velocity becomes zero momentarily. At this point, the distance of α particles from the center of the nucleus is known as the distance of closest approach (Fig. 5.8).

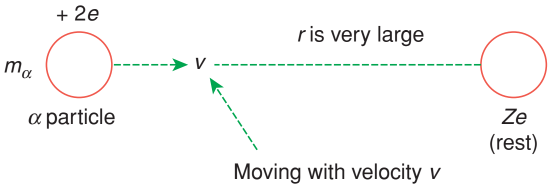


Figure 5.8 Determining distance of closest approach.

There are few assumptions in calculating the distance of closest approach.

1. There are no external forces acting on the system. Thus, the total energy (K.E. + P.E.) of the system is constant.
2. Initially the α particles are at a very large distance from the nucleus.

Calculation

Consider Fig. 5.9 as shown below.

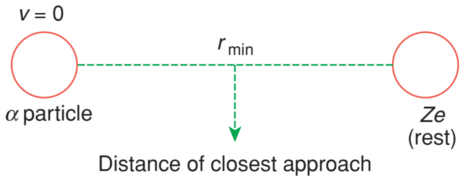


Figure 5.9 Distance of closest approach.

$$(\text{Total Energy})_i = (\text{K.E.})_i + (\text{P.E.})_i$$

$$= \frac{1}{2}mv^2 + \frac{K(2e)(Ze)}{r}$$

Therefore,

$$r_{\text{min}} = \frac{4kZe^2}{m_\alpha v^2}$$

On the basis of the observations and conclusions of his experiment, Rutherford proposed the nuclear model of an atom. The important postulates of this model were:

1. The positive charge and most of the mass of the atom is concentrated in a small region of the atom, which he called nucleus. The vast majority of the volume of an atom is, therefore, empty space.
2. The electrons surrounded the nucleus and moved at a high speed around the nucleus in circular paths called **orbits**. This part of atom outside the nucleus in which the electrons are distributed is known as extra-nuclear part.
3. The electrons and nucleus were held together by the electrostatic forces. Electrons do not collapse into the nucleus due to this force of attraction, because the revolving of electrons around the nucleus produces centrifugal force that balances the force of attraction.

Drawbacks of Rutherford Model

The nuclear model proposed for the atom by Rutherford can be visualized as a small-scale solar system in which the nucleus (heavy) is like the sun in the center with electrons (lighter) revolving around in orbits like planets. This model of the atom works reasonably well – in fact, it continues to be used to visualize a variety of chemical concepts. However, there are several drawbacks associated with this atomic model proposed by Rutherford and these are discussed as follows.

1. It could not explain the stability of the atom. According to this model, electrons revolve around the positively charged nucleus in circular orbits. According to Maxwell's classical electromagnetic theory, accelerated charged particles radiate energy. the negatively charged particle must be attracted towards the positively charged nucleus. Due to this attractive force, the radius of the circular path of the electrons must decrease continuously and ultimately the electron should fall into the nucleus. (Fig. 5.10) in 10^{-8} s. However, this does not actually happen and electrons do not fall into nucleus. Rutherford's model was not able to explain the stability of atoms.
2. It was not able to explain the line spectra for various elements.
3. This model was unable to explain the energies of electrons and their distribution around the nucleus.

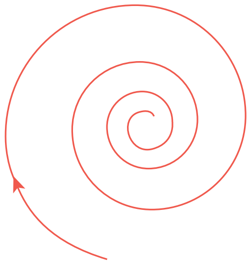


Figure 5.10 Decreasing radius of circular path of electrons.

Solved Example 5-1

Assume that a circle 1 cm in diameter is used to represent the nucleus of an atom. Calculate the size of the circle that would have to be used to represent the diameter of the atom.

Solution

According to Rutherford model, the radius of the nucleus is at least 10^4 times smaller than the radius of the atom. Given that radius of nucleus = 0.5 cm. Therefore the radius of atom = 0.5×10^4 cm. Hence, the diameter of the circle used to represent diameter of atom = 1×10^4 cm = 100 m.

Solved Example 5-2

With what velocity should an α-particle travel towards the nucleus of copper atom so that it arrives at a distance of 10^{-13} m from copper nucleus?

Solution

We have the relation

$$r_0 = \frac{1}{4\pi\epsilon_0} \times \frac{4Ze^2}{mv^2}$$

where r_0 is the distance of closest approach. Given that $r_0 = 10^{-13}$ m and Z for copper = 29. Substituting these values and $e = -1.6 \times 10^{-19}$ C, $m = 4 \times 1.67 \times 10^{-27}$ kg and $8.85 \times 10^{12}\ \mathrm{C^2\,N^{-1}\,m^{-2}}$, we get

$$10^{-13} = \frac{1}{4\times 3.14\times 8.85\times 10^{-12}} \times \frac{4\times 29\times (1.6\times 10^{-19})^2}{4\times 1.67\times 10^{-27}\times v^2}$$

$$v^2 = 2\times 0.199\times 10^{-14}\ \mathrm{m^2\,s^{-2}} \Rightarrow v = 6.30\times 10^{-8}\ \mathrm{m\,s^{-1}}$$

Solved Example 5-3

Nuclear radius is of the order of 10^{-13} cm while atomic radius is of the order of 10^{-8} cm. Assuming the nucleus and the atom to be spherical, what fraction of the atomic volume is occupied by the nucleus?

Solution

Fraction of atomic volume occupied by a nucleus =

$$\frac{\text{Nuclear volume}}{\text{Atomic volume}} = \frac{4/3\pi(10^{-13})^3}{4/3\pi(10^{-8})^3} = 10^{-15}$$

5.5 | REPRESENTATION OF ATOM WITH ELECTRONS AND NEUTRONS

In 1913, Moseley studied the frequencies of the X-rays given off when the electrons in the cathode ray tube strike the anode made with different elements. He found that wavelength of X-ray decreases in the regular way on moving from the lighter to heavier element. He formulated the relationship as Moseley's law and expressed it mathematically as

$$\nu \propto (Z-1)^2 \quad \text{or} \quad \sqrt{\nu} = a(Z-b)$$

where a and b are constants and Z is the atomic number. He concluded that since the frequencies of the X-ray emitted depend on the charge on the nucleus; therefore, Z is a fundamental property of an atom and named it as *atomic number*. It was equal to the positive charge (charge on nucleus) of an atom.

To understand the representation of atoms with protons, neutrons and electrons, let us consider the atoms of the element copper. Most atoms are composed of a nucleus containing a total of 63 nucleons (protons and neutrons), of which 29 are protons and 34 are neutrons. The atom also contains 29 electrons that exactly balance the positive charge of the protons, resulting in a neutral atom. The number of protons in the nucleus (which is equal to the total positive charge) is the atom's **atomic number (*Z*)**. It is also equal to the number of electrons in the neutral atom. The total number of nucleons (protons and neutrons) is called the **mass number (*A*)**. Therefore, this particular copper atom has an atomic number of 29 and a mass number of 63. An atom can be represented as ${}^{A}_{Z}\mathrm{X}$ where X represents the symbol of the element, and A and Z represent the mass number and atomic number, respectively.

Isobars and Isotopes

The atoms which have same mass number but different atomic numbers are called **isobars**. There are other copper atoms that are not exactly the same, however. These atoms of copper have a mass number of 65 rather than 63. This means that these atoms have 36 neutrons as well as 29 protons. An atom of a specific element with a specific mass number is known as an **isotope**. The isotopes of an element have the same atomic number but different mass numbers. The difference in isotopes exists because of the difference in the number of neutrons. Carbon, for example, has three naturally occurring isotopes: ^{12}C, ^{13}C and ^{14}C. Now, ^{12}C has 6 protons and 6 neutrons; ^{13}C has 6 protons and 7 neutrons; ^{14}C has 6 protons and 8 neutrons.

Note: The graphite in a pencil contains a mixture of ^{12}C, ^{13}C and ^{14}C atoms. The three isotopes, however, do not occur to the same extent. Most of the atoms (98.892%) are ^{12}C, a small percentage (1.108%) is ^{13}C, and only about 1 in 10^{12} is the radioactive isotope of carbon, ^{14}C. The percentage of atoms occurring as a given isotope is referred to as the **natural abundance** of that isotope.

Most elements that are present in nature exist as a mixture of isotopes. *It is the atomic number, however, that distinguishes one element from another*. Any atom with an atomic number of 29, regardless of any other consideration, is an atom of copper. If the atomic number is 28, the element is nickel; if it is 30, the element is zinc.

Specific isotopes are written in a form known as *isotopic notation*. In isotopic notation, the mass number is written as a superscript to the left of the element. Sometimes, the atomic number is written as a subscript, also on the left.

Note: The chemical properties are dependent on the number of electrons which in turn depends on the number of protons. The number of protons in the nucleus of an atom determines the identity of the atom. So, all isotopes show similar chemical properties. As a result, all atoms of an element must have the same number of protons. But they do not have to contain the same number of neutrons.

Atoms or ions containing same number of electrons are called **isoelectronic** species. For example, F^-, Na^+, Mg^{2+}, Al^{3+}, Ne.

Isotones, Isodiaphers and Nuclear Isomers

Two nuclei having the same number of neutrons or same value of $(A-Z)$ are called **isotones** they differ in their atomic number and mass number but contain the same number of neutrons. For example, ${}^{12}_{5}B$ and ${}^{13}_{6}C$ are isotones.

Element	${}^{12}_{5}B$	${}^{13}_{6}C$
A	12	13
Z	5	6
$A-Z$	7	7

Two nuclei with the same difference between number of neutrons and protons or having same value of $(A-Z)-Z$ or $(A-2Z)$ are called **isodiaphers**. For example, ${}^{234}_{90}Th$ and ${}^{238}_{92}U$ are isodiaphers.

Element	${}^{234}_{90}Th$	${}^{238}_{92}U$
A	234	238
Z	90	92
$A-2Z$	54	54

When two nuclei have the same A and Z but different characteristics, they are called **nuclear isomers**. For example, ${}^{14}_{7}N$ and ${}^{14}_{7}C$ are nuclear isomers.

Solved Example 5-4

The number of electrons, protons and neutrons in a species are equal to 18, 16 and 16, respectively. Assign the proper symbol to the species.

Solution

The atomic number is equal to number of protons = 16. The element is sulphur (S).

Atomic mass number = number of protons + number of neutrons

$$= 16 + 16 = 32.$$

Species is not neutral as the number of protons is not equal to electrons. It is an anion (negatively charged) with charge equal to excess electrons = 18 – 16 = 2.

So, symbol is ${}^{32}_{16}S^{2-}$.

Note: Before using the notation $^{A}_{Z}X$, find out whether the species is a neutral atom, a cation or an anion. If it is a neutral atom, equation is valid, that is, number of protons = number of electrons = atomic number. If the species is an ion, determine whether the number of protons are larger (cation, positive ion) or smaller (anion, negative ion) than the number of electrons is always given by $A - Z$ whether the species is neutral or ion.

Solved Example 5-5

Naturally occurring boron consists of two isotopes whose atomic weights are 10.01 and 11.01. The atomic weight of natural boron is 10.81. Calculate the percentage of each isotope in natural boron. **(IIT-JEE 1978)**

Solution

Average mass = Mass of isotope A × Mole fraction of A + Mass of isotope B × Mole fraction of B

$$10.81 = 11.01x + 10.01\,(1 - x)$$
$$\Rightarrow 10.81 = 11.01x + 10.01 - 10.01x$$
$$x = 10.81 - 10.01 = 0.80$$

Therefore, the percentage of each isotope in natural boron is 80%.

Solved Example 5-6

$^{234}_{92}X \xrightarrow[+6\beta]{-7\alpha} Y$. Find out the atomic number, mass number of Y and identify the isotope. **(IIT-JEE 2004)**

Solution

As per the reaction, the mass number of Y = 234 − 7 × 4 (from α particle) + 6 × 0 (from β particle) = 206.

The atomic number of Y = 92 − 7 × 2 (from α-particle) + 6 × 1 (from β particle) = 84. Hence, the isotope is $^{206}_{84}Po$.

Solved Example 5-7

Calculate the number of protons and neutrons in the nucleus and the number of electrons surrounding the nucleus of a $^{39}_{19}K$ atom. What are the atomic number and the mass number of this atom?

Solution

The atomic number and mass number are calculated as follows:

Atomic number = Number of protons = 19
Mass number = Protons + neutrons
= 19 + 20 = 39

Solved Example 5-8

The relative atomic mass of an element is found to be 35.5. There are two isotopes of chlorine $^{37}_{17}Cl$ and $^{35}_{17}Cl$. What is the percentage of these two isotopes in the element?

Solution

Let the percentage of isotope $^{37}_{17}Cl$ be x, then the percentage of the isotope $^{35}_{17}Cl$ is $(100 - x)$. Then the average mass is given by

$$\left(37 \times \frac{x}{100}\right) + \left(35 \times \frac{100 - x}{100}\right) = 35.5$$
$$37x + 3500 - 35x = 3550 \Rightarrow x = 25$$

Therefore, percentage of $^{37}_{17}Cl$ is 25% and that of $^{35}_{17}Cl$ is 75%.

Solved Example 5-9

Write the symbols of the isotopes that contain the following. (Use the periodic table of atomic masses and numbers for additional information, as needed.)

(a) An isotope of iodine whose atoms have 78 neutrons.

(b) An isotope of strontium whose atoms have 52 neutrons.

(c) An isotope of caesium whose atoms have 82 neutrons.

(d) An isotope of fluorine whose atoms have 9 neutrons.

Solution

(a) ${}^{131}_{53}\text{I}$, **(b)** ${}^{90}_{38}\text{Sr}$, **(c)** ${}^{137}_{55}\text{Cs}$, **(d)** ${}^{18}_{9}\text{F}$

Solved Example 5-10

How many nucleons are present in an atom of Nobelium, ${}^{254}_{102}\text{No}$?

Solution

Nucleons are particles that make up the atomic nucleus and include the protons, each of which carries a single unit of positive charge (charge = +1), and neutrons (no charge). Hence,

Number of nucleons present in ${}^{254}_{102}\text{No} = 254$

5.6 | NATURE OF WAVES

Consider the displacement (oscillation) of a particle by transfer of energy as shown in Fig. 5.11. Then the related terms are defined as:

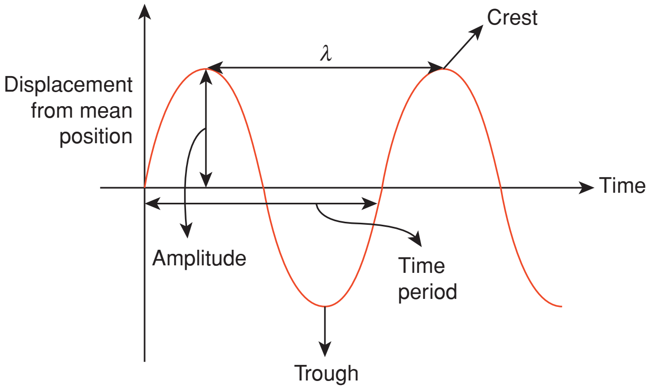


Figure 5.11 Displacement of a particle (oscillator) from the mean position as a function of time.

Wave: An oscillation accompanied by a transfer of energy that travels through space and mass.
Wavelength: Wavelength can be defined as the distance between two maxima of a wave. It is expressed in meters. It is denoted by λ.
Frequency: It is defined as the number of waves that pass a fixed point in unit time. It is expressed in s^{-1} or Hz. It is denoted by ν.
Wavenumber: It is defined as the number of waves per unit distance. It is reciprocal of wavelength. It is denoted by $\bar{\nu}$.
Time period: The time taken for completion of one wave. It is expressed in s (second). It is denoted by T.
Amplitude: It is defined as the maximum displacement of a wave from its mean position.

5.7 | NATURE OF ELECTROMAGNETIC RADIATION

Rutherford's model assumes that most of the mass and all of the positive charge of an atom are concentrated in an infinitesimally small nucleus surrounded by a sea of lightweight, negatively charged electrons. The next step in understanding the structure of atom was to visualize how these electrons are distributed around the nucleus. Much of the understanding about the arrangement of electrons in an atom is based on the studies carried out on the interaction between matter and different forms of **electromagnetic radiation**. Neils Bohr, a Danish physicist, improved the model proposed by Rutherford based on the dual character of the electromagnetic radiation (having some of the properties of both a particle and a wave) and on atomic spectra.

Wave Nature of Electromagnetic Radiation

A series of groundbreaking experiments showed that classical physics does not correctly describe energy transfer by electromagnetic radiation. In 1870, Max Planck (1858–1947), a German physicist, proposed that electromagnetic radiation can be viewed as a stream of tiny packets or **quanta** of energy that were later called **photons**. Scientists divide matter into two categories, particles and waves. **Particles** are easy to understand because they have a measurable mass and they occupy space. **Waves** on the other hand have no mass and yet they carry energy as they travel through space.

In the case of electromagnetic radiation, the disturbance can be a vibrating electric charge. When the charge oscillates, it produces a pulse in the electric field around it. As the electric field pulses, it creates a pulse in the magnetic field. The magnetic field pulse gives rise to yet another electric field pulse further away from the disturbance. The process continues, with a pulse in one field giving rise to a pulse in the other, and the resulting train of pulses in the electric and magnetic fields is called an **electromagnetic wave**. When an electromagnetic wave passes an object, the oscillating electric and magnetic fields may interact with it. A tiny charged particle placed in the path of the wave will be moved back and forth by the oscillating electric and magnetic fields (Fig. 5.12). Thus, according to the electromagnetic wave theory, light is an electromagnetic wave consisting of electric and magnetic fields with continuous distribution of energy over the region in which the wave extends.

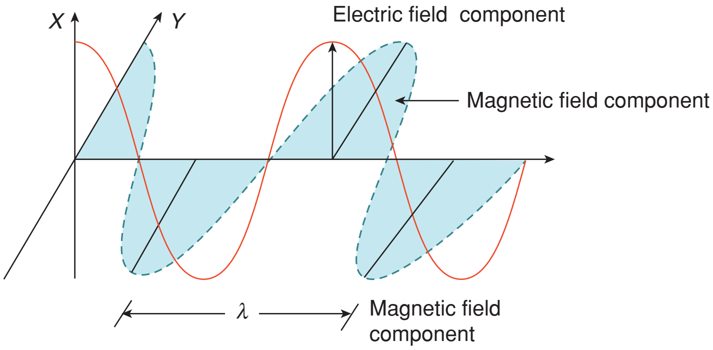


Figure 5.12 The electric and magnetic field components of an electromagnetic wave vibrating in two mutually perpendicular planes. The wavelength (λ), frequency, speed and amplitude of both the components is the same.

The energy associated with regions of the electromagnetic spectrum is related to wavelengths and frequency by the equation:

$$E = h\nu = \frac{hc}{\lambda}$$

where E = energy of the radiation in joules; h = Planck's constant, 6.626×10^{-34} J s; ν = frequency of radiation in Hz and c = velocity of light, 2.998×10^{8} m s^{-1}.

Light is one form of electromagnetic radiation and is usually classified by its wavelength, as shown in Fig. 5.13.

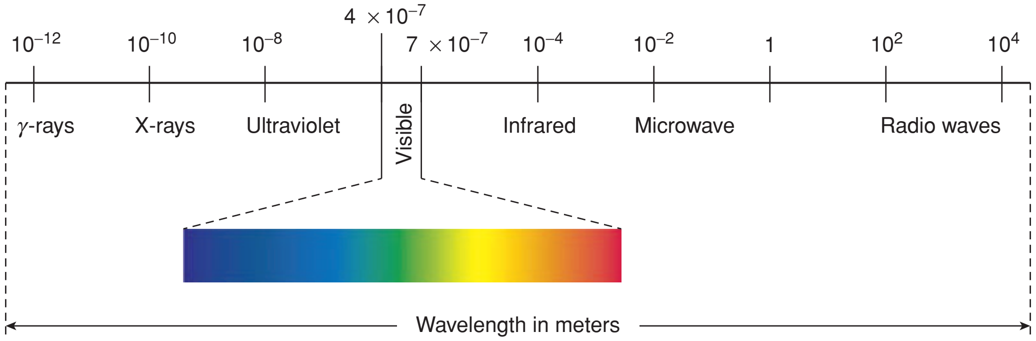


Figure 5.13 The electromagnetic spectrum.

Solved Example 5-11

Calculate the frequency of red light that has a wavelength of 700.0 nm if the speed of light is 3×10^8 m s^{-1}.

Solution

The product of the frequency times the wavelength of any wave is equal to the speed with which the wave travels through space. In this case, the wave travels at the speed of light: 3×10^8 m s^{-1}. Before we can calculate the frequency of the radiation, we have to convert the wavelength into units of meters.

$$700 \text{ nm} \times \frac{1 \text{ m}}{10^9 \text{ nm}} = 7.0 \times 10^{-7} \text{ m}$$

We can then substitute this wavelength and the speed of light into the following equation: $\nu\lambda = c$.

$$\nu(7.0 \times 10^{-7} \text{ m}) = 3 \times 10^8 \text{ m s}^{-1}$$

We can then solve for the frequency of the light in units of cycles per second.

$$\nu = 4.285 \times 10^{14} \text{ s}^{-1}$$

Solved Example 5-12

The frequency of red line in the spectrum of potassium is 3.91×10^{14} s^{-1}. Calculate the wavelength of this light in meters and nanometers.

Solution

The wavelength can be calculated as

$$\lambda = \frac{c}{\nu} = \frac{3 \times 10^8}{3.91 \times 10^{14}} = 7.67 \times 10^{-7} \text{ m} = 767 \text{ nm}$$

Solved Example 5-13

An octave in a musical scale corresponds to a change in the frequency of a note by a factor of 2. If a note with a frequency of 440 Hz is an "A", then the "A" one octave above this note has a frequency of 880 Hz. What happens to the wavelength of the sound as the frequency increases by a factor of 2? What happens to the speed at which the sound travels to your ear?

Solution

As the frequency increased by a factor of 2, the wavelength is decreased by a factor of 2. The speed at which the sound travels to your ear remains constant at 340 m s^{-1}.

Solved Example 5-14

An electron is moving with wavelength 590 nm; calculate potential with which electron is accelerated.

Solution

The potential is calculated as

$$E = \frac{hc}{\lambda} = \frac{6.626\times10^{-34}\times3\times10^{8}}{590\times10^{-9}} = 3.369\times10^{-19}\ \text{J}$$

Now,

$$eV = 3.368\times10^{-19}$$

or

$$V = \frac{3.369\times10^{-19}}{1.6\times10^{-19}} = 2.1056\ \text{V}$$

5.8 | PLANCK'S QUANTUM THEORY

According to Planck's quantum theory, energy of each electromagnetic wave is limited to discrete value and cannot be varied arbitrarily. This proposal contradicts classical physics according to which each oscillator has a fixed mean value of energy KT.

According to Planck's theory, energy is emitted or absorbed in the form of small packets. Each packet is known as *quantum*. In case of the electromagnetic radiation being light, this quantum of energy is known as photon.

If energy of one packet = E_1, it was observed that

$$E_1 \propto \nu \qquad \text{(Frequency of electromagnetic wave)}$$

$$E_1 = h\nu$$

where h is the Planck's constant (6.626×10^{-34} Js).

If we have n photons with total energy E, then,

$$E = n(h\nu) = n\left(\frac{hc}{\lambda}\right)$$

where $n = 0, 1, 2, 3, \ldots$

This is known as the quantization of energy.

Blackbody Radiation

It was observed by the physicists that when solids are heated, they emit radiation over a wide range of wavelengths. For example, when an iron rod is heated in the furnace, it progressively changes to a stronger red color, then becomes white and turns blue when heated to even higher temperature. In terms of frequency, it implies that on progressive heating, the frequency of energy emitted by the object rises from a lower to a higher value with increase in temperature. A body which can emit or absorb radiation of all frequencies is known as **blackbody** and the radiation emitted by it is known as **blackbody radiation**.

At a given temperature, the spectral emissive power, of light emitted by a blackbody depends on the wavelength emitted. At a given temperature, the intensity of radiation emitted increases with increase of wavelength, reaches a maximum value and then decreases with further increase in wavelength. Furthermore, Wein found out that if we increase the temperature of the blackbody, the wavelength corresponding to the most intense radiation decreases. Both these observations are illustrated graphically in Fig. 5.14.

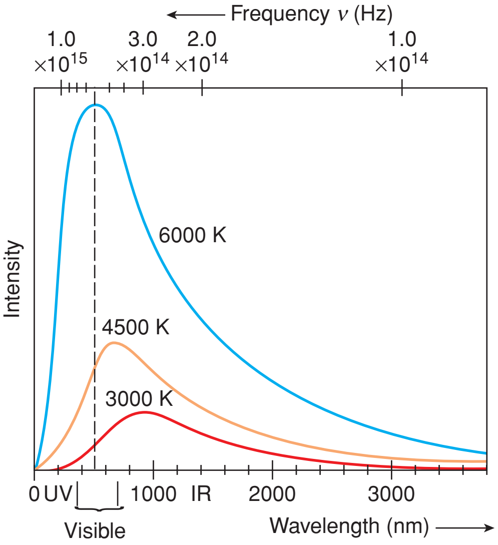


Figure 5.14 Intensity of radiation emitted as a function of wavelength or frequency at three different temperatures.

The first explanation for blackbody radiation was given by Max Planck. According to Planck's quantum theory, energy is not continuous but is discrete. The smallest quantity of this energy is called quantum. The energy can be given as $E = h\nu$. This means that energy occurs in "packets" called quanta, of magnitude $h/2\pi$, where h is Planck's constant and its value is 6.626×10^{34} J s. With this theory, Planck was able to explain the distribution of intensity of radiation emitted by a blackbody as a function of wavelength or frequency at a given temperature.

5.9 | SPECTRA – CONTINUOUS AND DISCONTINUOUS SPECTRUM

Atomic Spectra

A spectrum is formed when the light from an object that has been heated to a very high temperature (such as the filament in an electric light bulb) is split by a prism and displayed on a screen. A rainbow after a summer shower appears as a continuous spectrum that most people have seen. In this case, tiny water droplets in the air spread out the colors contained in sunlight. A visible spectrum is called a **continuous spectrum** (ranging from 7.5×10^{14} Hz for violet to 4×10^{14} Hz for red) because it contains a continuous unbroken distribution of light of *all* colors. The red light with the longest wavelength deviates the least, while the violet light with the shortest wavelength deviates the most.

When electromagnetic radiation interacts with matter in form of atoms, molecules or ions, these absorb energy and are raised to higher energy level. When they return to the more stable ground state, the atoms and molecules emit energy in various regions of electromagnetic spectrum. The atoms of the given element always undergo the same specific energy changes; this is because electrons can have only certain definitive amounts of energy. Hence, the energy at electronic level is quantized.

Emission and Absorption Spectra

The spectrum of radiation emitted by a substance that has adsorbed electromagnetic radiation is known as an emission spectrum. To obtain an **emission spectrum**, a sample is either heated in a flame or irradiated with a beam of light, the atoms/molecules/ions of the sample absorb the energy from the radiation and are raised to unstable excited state. They revert to the more stable lower energy state by losing the absorbed energy and emitting radiations of specific wavelengths which are recorded as the emission spectrum. When the radiation is passed through a sample, it absorbs certain wavelengths. When the continuous spectrum is observed, there are a few dark spaces which represent the radiation that is absorbed by the matter. This is called **absorption spectrum**.

Spectroscopy is a study of either the radiation absorbed or the radiation emitted. Atomic spectroscopy is an important technique for studying the energy and the arrangement of electrons in atoms. When a narrow beam of this light is passed through a prism, as shown in Fig. 5.15, we do *not* see a continuous spectrum. Instead, only a few colors are observed, displayed as a series of individual lines. This series of lines is called the element's **atomic spectrum** or **emission spectrum**. The emission spectra of visible light are continuous, but that of gaseous atoms contain lines with dark spaces between them. This is called **line spectra**.

Because the light corresponding to the individual emissions appears as lines on the screen. This spectrum is also known as discontinuous spectrum.

Figure 5.16 shows the visible portions of the atomic spectra of hydrogen spectrum has five lines in the visible region of the electromagnetic spectrum – red, green, blue, violet1 and violet2. But Balmer could see only four lines and a continuum.

In fact, each element has its own unique atomic spectrum that is as characteristic as a fingerprint, and can be used to identify the element.

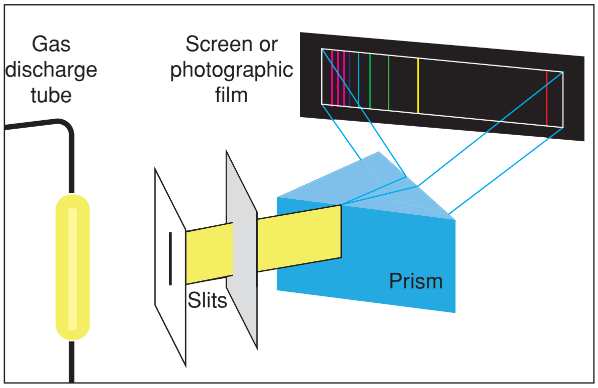


Figure 5.15 Production and observation of an atomic spectrum.

Note: This atomic spectrum was first used in identification of unknown atoms by Robert Bunsen, a German chemist. Chemists and physicists began using the spectroscope to catalog the wavelength of light emitted or absorbed by a variety of compounds and used this data to detect the presence of certain elements in minerals and in sunlight. This led to discovery of many new elements, such as rubidium, caesium, gallium, thallium, indium and scandium from their minerals and helium from sunlight.

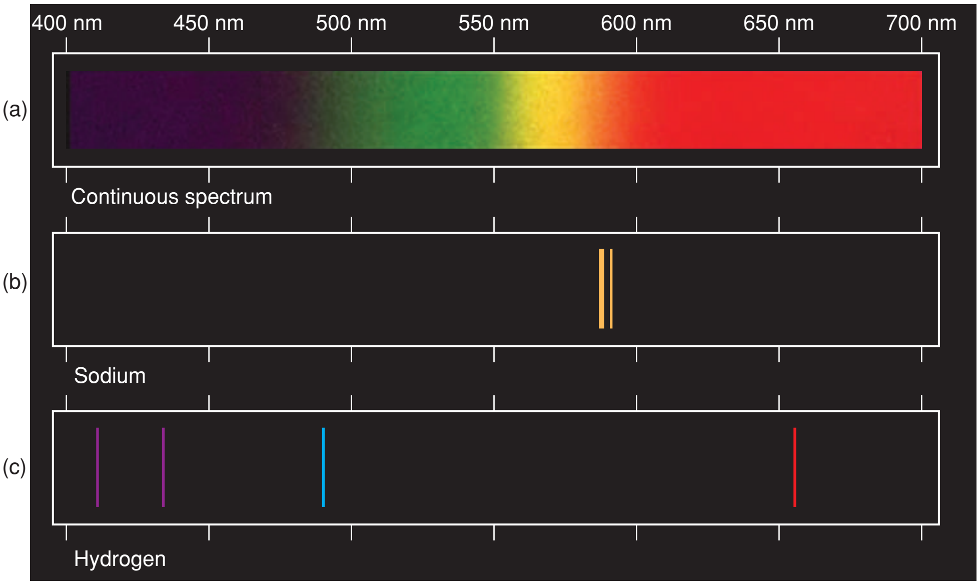


Figure 5.16 Atomic spectrum (line spectrum) produced by hydrogen.

Note: For some elements with higher values of Z ($Z > 20$), we will have closely spaced lines known as bands and we will thus get a band spectrum instead of a line spectrum. Band spectrum is also a discontinuous spectrum.

5.10 | BOHR'S MODEL FOR HYDROGEN ATOM

In 1913, working further on Rutherford's model for atomic nucleus, Niels Bohr suggested that the atomic nucleus was surrounded by electrons moving in orbits like planets round the sun. He was awarded the Nobel Prize for Physics in 1922 for his work on the structure of the atom.

Bohr's Postulates

Bohr's model of atom is based on the following postulates:

1. The electron moves around the nucleus in orbits (arranged concentrically around the nucleus). These orbitals have a fixed radius and energy. An electron does not radiate energy if it stays in one orbit, and therefore does not slow down.
2. When an electron is moving in an circular orbit it experiences a centripetal acceleration of v^2/r. Since an electron is experiencing an attractive force from the nucleus $= \frac{kZe^2}{r^2}$. Therefore,

$$\frac{mv^2}{r} = \frac{kZe^2}{r^2}.$$

Number of revolutions of electron per second $= \frac{v}{2\pi r}$.

3. When an electron remains in its orbit or stationary state, the angular momentum is given by

$$m_e vr = \frac{nh}{2\pi}$$

where $n = 1, 2, 3, \ldots$. Thus an electron can move only in those orbits for which the angular momentum is an integral multiple of $h/2\pi$. Hence, only certain fixed orbits are permitted around the nucleus in an atom.

4. It is applicable only for single electron species
5. The integral numbers $n = 1, 2, 3, \ldots$, are the principal quantum numbers and correspond to permitted stationary states for electron in an atom..
6. The difference in energy observed when the frequency of radiation is absorbed or emitted is given by the Bohr frequency rule, as shown in Fig. 5.17.

$$\nu = \frac{\Delta E}{h} = \frac{E_2 - E_1}{h}$$

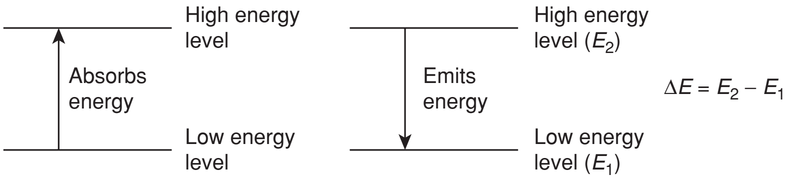


Figure 5.17 Absorption and emission of energy.

Bohr's model for hydrogen could successfully predict the radius of Bohr orbit, the velocity of electron in an orbit and the energy associated with an electron in each energy level. It could be extended to predict these parameters for hydrogen-like species

Radius of Bohr Orbits in Hydrogen

The radius of the stationary states is known as **Bohr radius** and the radius of stationary state in hydrogen atom can be calculated as follows.

$$\Delta E = E_2 - E_1$$

For an electron to remain in its orbit, the electrostatic attraction between the electron and the nucleus which tends to pull the electron towards the nucleus must be equal to the centrifugal force which tends to throw the electron out of its orbit.

$$\text{Centrifugal force} = \frac{m_e v^2}{r}$$

If the charge on the electron is e, the number of charges on the nucleus Z, and the permittivity of a vacuum $\in_0$, then

$$\text{Coulombic attractive force} = \frac{Ze^2}{4\pi\in_0 r^2} = \frac{kZe^2}{r^2}$$

where constant $k = 1/4\pi\in_0 = 8.988 \times 10^9$ Nm/C^2.

So, $$\frac{m_e v^2}{r} = \frac{Ze^2}{4\pi\in_0 r^2} \quad (5.1)$$

Hence, $$v^2 = \frac{Ze^2}{4\pi\in_0 m_e r} = \frac{kZe^2}{m_e r} \quad (5.2)$$

According to Planck's quantum theory, energy is not continuous but is discrete. This means that energy occurs in "packets" called quanta. The angular momentum m_evr, of an electron in orbit must be equal to a whole number n multiple of $h/2\pi$.

$$m_evr = \frac{nh}{2\pi}$$

$$v = \frac{nh}{2\pi m_e r} \Rightarrow v^2 = \frac{n^2h^2}{4\pi^2 m_e^2 r^2} \tag{5.3}$$

Combining Eq. (5.3) with Eq. (5.2), we get

$$\frac{Ze^2}{4\pi \in_0 m_e r} = \frac{n^2h^2}{4\pi^2 m_e^2 r^2} \quad \text{or} \quad \frac{kZe^2}{m_e r} = \frac{n^2h^2}{4\pi^2 m_e^2 r^2}$$

$$\frac{kZe^2}{r} = m_e \times \frac{n^2h^2}{4\pi^2 m_e^2 r^2}$$

Hence,

$$r = \frac{\in_0 n^2 h^2}{\pi m_e^2 Z} \quad \text{or} \quad \frac{n^2}{Z}\left(\frac{h^2}{4\pi^2 k m_e e^2}\right) \tag{5.4}$$

For hydrogen the charge on the nucleus $Z = 1$, and if $n = 1$ this gives a value $r = 1^2 \times 0.0529$ nm and for $n = 2$, $r = 2^2 \times 0.0529$ nm. In general, $r_n = n^2a_0$, where $a_0 = 0.0529$ nm. This gives a picture of the hydrogen atom where an electron moves in circular orbits of radius proportional to $1^2, 2^2, 3^2, \ldots$. Thus, Bohr radius can be expressed as $r_n = n^2a_0$, where $a_0 = 52.9$ pm. The Bohr radius of first stationary state is 52.9 pm and the electron is generally found in this orbit.

From Eq. 5.4, we have

$$r = r_0 \times \frac{n^2}{Z}$$

where $r_0 = 0.529$ Å.

Thus,

$$r \propto \frac{1}{m}$$

Velocity of Electron

The velocity of electron moving in the orbit is given by the expression

$$v = \frac{nh}{2\pi m_e r} = \frac{nh}{2\pi m_e} \times \frac{4\pi^2 Zkm_e e^2}{n^2h^2} = \frac{2\pi Zke^2}{nh} = \frac{Ze^2}{2\in_0 nh}$$

$$v = \frac{Z}{n} = (2.18 \times 10^6\,\text{ms}^{-1}) = \left(\frac{Z}{n}\right)v_0$$

$$v_0 = 2.18 \times 10^6\,\text{ms}^{-1}$$

Thus v is independant of m.

Energy of Electron in Hydrogen Atom

For hydrogen atom, the energy associated with an electron in the stationary state in which it is present can be obtained by using the value of Bohr radius and is calculated as follows.

The total energy of an electron in a one-electron system = Kinetic energy + Potential energy. The kinetic energy of the electron is

$$\text{K.E.} = \frac{1}{2}m_e v^2 \tag{5.5}$$

The potential energy of an electron at an infinite distance from the nucleus is taken to be zero. The potential energy of the electron at a distance *r* from the nucleus is the work done in moving the electron from infinity to the point which is at a distance *r* from the nucleus. We know that the coulombic attractive force is given by

$$F = -\left(\frac{1}{4\pi\epsilon_0}\right)\left(\frac{Ze^2}{r^2}\right) = -\left(\frac{Ze^2}{4\pi\epsilon_0 r^2}\right)$$

Therefore, to find the work done by this variable force, we find the work done in moving the electron through an infinitesimally small distance (over which the force may be assumed to be constant) and integrating over the entire distance. The work done in moving through small distance d*r* is given by

$$\mathrm{d}w = F\mathrm{d}r = \left(\frac{Ze^2}{4\pi\epsilon_0}\right)\left(\frac{1}{r^2}\right)\mathrm{d}r$$

The total work done in moving the electron from infinity to the point at a distance *r* from the nucleus is given by the integral

$$W = \int \mathrm{d}w = \int_{r=\infty}^{r=r}\left(\frac{Ze^2}{4\pi\epsilon_0}\right)\left(\frac{1}{r^2}\right)\mathrm{d}r = -\frac{Ze^2}{4\pi\epsilon_0 r} \tag{5.6}$$

The total energy of the electron is kinetic energy + potential energy

$$E_{\text{total}} = \text{K.E.} + \text{P.E}$$

From Eqs. (5.6) and (5.5), we get

$$E_{\text{total}} = \frac{1}{2}m_e v^2 + \left(-\frac{Ze^2}{4\pi\epsilon_0 r}\right) \tag{5.7}$$

From Eq. (5.1), we have

$$\frac{m_e v^2}{r} = \frac{Ze^2}{4\pi\epsilon_0 r^2} \text{ or } \frac{kZe^2}{r^2} \Rightarrow m_e v^2 = \frac{Ze^2}{4\pi\epsilon_0 r} \text{ or } \frac{kZe^2}{r}$$

Substituting in Eq. (5.6), we get

$$E_{\text{total}} = \frac{1}{2}\left(\frac{Ze^2}{4\pi\epsilon_0 r}\right) + \left(-\frac{Ze^2}{4\pi\epsilon_0 r}\right) \text{ or } \frac{1}{2}\left(\frac{kZe^2}{r}\right) + \left(\frac{-kZe^2}{r}\right)$$

Substituting value of *r* from Eq. (5.4), we get

$$E_{\text{total}} = \frac{-Z^2 m_e e^4}{8n^2 h^2 \epsilon_0^2} \tag{5.8}$$

Note: We know that

$$\text{T.E.} = \text{K.E.} + \text{P.E.}$$

where T.E. is total energy, K.E. is kinetic energy and P.E. is the potential energy.

$$\text{K.E.} = \frac{1}{2}\left(\frac{kZe^2}{r}\right) \tag{5.9}$$

$$\text{P.E.} = -\frac{kZe^2}{r} \tag{5.10}$$

From Eq. (5.9) and (5.10), if we assume K.E. be *x*, then

$$\text{P.E.} = -2x$$

Also,

$$\begin{aligned}\text{T.E} &= \text{K.E} + \text{P.E} \\ &= x + (-2x) = x - 2x \\ &= -x\end{aligned}$$

Thus, if K.E. = x, then P.E. = $2x$ and T.E. = $-x$

For an atom of hydrogen, Z = 1, $m_e = 9.11 \times 10^{-31}$ kg, $e = 1.6 \times 10^{-19}$ C, $\in_0 = 8.85 \times 10^{-12}$ C^{2}N^{-1}m^{-2}, $h = 6.626 \times 10^{-34}$ J s.

Substituting these values in Eq. (5.7), we get

$$E = \left(\frac{-1 \times 9.11 \times 10^{-31} \times (1.6 \times 10^{-19})^4}{8 \times n^2 \times (6.626 \times 10^{-34})^2 \times (8.85 \times 10^{-12})^2}\right) = \left(\frac{-2.18 \times 10^{-18}}{n^2}\right) \text{J} = \frac{-13.6}{n^2} \text{eV} = -13.6 \text{ eV} \times \frac{Z^2}{n^2} \quad (\text{for } Z \neq 1)$$

therefore $E \propto m$.

The energy of the electron in the stationary state n_1 and n_2 in an atom of hydrogen are given by

$$E_1 = \left(\frac{-2.18 \times 10^{-18}}{(n_1)^2}\right) \text{J atom}^{-1} \quad \text{and} \quad E_2 = \left(\frac{-2.18 \times 10^{-18}}{(n_2)^2}\right) \text{J atom}^{-1}$$

Thus, the energy of electron is given by the expression

$$E_n = -R_\text{H}\left(\frac{1}{n^2}\right) \quad n = 1, 2, 3, \ldots$$

where R_H is the Rydberg constant for hydrogen and its value is 2.18×10^{-18} J. Energy for first orbit or the ground state is

$$E_1 = -2.18 \times 10^{-18}\left(\frac{1}{1^2}\right) = -2.18 \times 10^{-18} \text{ J}$$

Energy for the second orbit is

$$E_2 = -2.18 \times 10^{-18}\left(\frac{1}{2^2}\right) = -0.545 \times 10^{-18} \text{ J}$$

The energy diagram, depicting energies of different stationary state is given in Fig. 5.18.

Note that a free electron corresponds to being present in orbit $n = \infty$ and is infinitely away from the nucleus, and thus, its energy is taken as zero. When the electron is present in any other stationary state (orbit) n, it is attracted to the nucleus and its energy is lowered. The energy of electron in orbit n is thus larger in absolute value than zero, but is denoted with a negative sign, since it is being lowered. The negative sign for the energy thus represents the relative stability of the state with reference to zero energy state $n = \infty$.

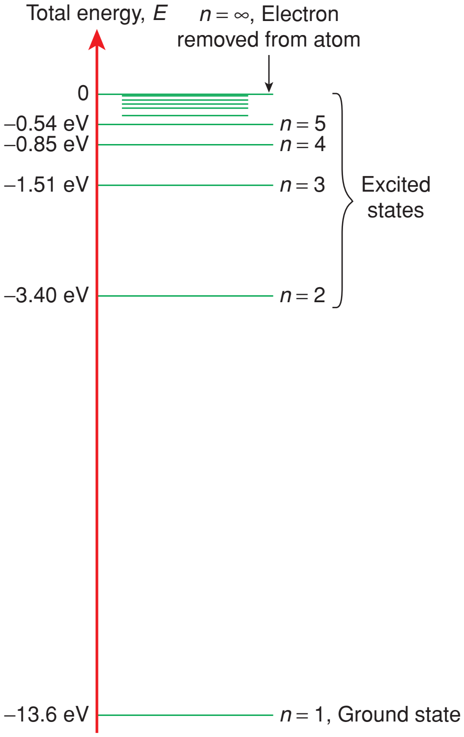


Figure 5.18 Energy level diagram for hydrogen atom.

The line spectrum observed for hydrogen can be explained quantitatively using Bohr's model. The various lines obtained in the spectrum can be related to transition between different energy states. When an electron undergoes a transition from initial state n_i to final state n_f, the energy change is given by

$$\Delta E = E_2 - E_1 = 2.18 \times 10^{-18}\left(\frac{1}{(n_\text{f})^2} - \frac{1}{(n_\text{i})^2}\right) \text{J atom}^{-1} \tag{5.11}$$

When the electron moves from the stationary state n_2 to the stationary state n_1, the energy it releases will be

$$\Delta E = E_2 - E_1 = 2.18 \times 10^{-18}\left(\frac{1}{(n_1)^2} - \frac{1}{(n_2)^2}\right) \text{J atom}^{-1}$$

Therefore, the frequency of the radiation emitted during the transition of the electron is

$$\nu = \left(\frac{\Delta E}{h}\right) = \left(\frac{2.18\times10^{-18}}{6.626\times10^{-34}}\right)\left(\frac{1}{(n_1)^2}-\frac{1}{(n_2)^2}\right) = 3.29\times10^{15}\left(\frac{1}{(n_1)^2}-\frac{1}{(n_2)^2}\right)\text{ Hz}$$

This is the equation given by J.J. Balmer while studying the hydrogen spectrum.

$$\nu = \frac{c}{\lambda}$$

Therefore,

$$\frac{c}{\lambda} = 3.29\times10^{15}\left(\frac{1}{(n_1)^2}-\frac{1}{(n_2)^2}\right)\text{ Hz}$$

Now,

$$\frac{1}{\lambda} = \left(\frac{3.29\times10^{15}}{c}\right)\left(\frac{1}{(n_1)^2}-\frac{1}{(n_2)^2}\right)\text{ m}^{-1}$$

where $1/\lambda = 1/\nu = \bar{\nu}$ wave number, that is, the number of waves in 1 m.

$$\bar{\nu} = \frac{1}{\lambda} = \left(\frac{3.29\times10^{15}}{3.0\times10^{8}}\right)\left(\frac{1}{(n_1)^2}-\frac{1}{(n_2)^2}\right)\text{ m}^{-1} = 1.09677\times10^{7}\left(\frac{1}{(n_1)^2}-\frac{1}{(n_2)^2}\right)\text{ m}^{-1}$$

where 1.09677×10^7 m^{-1} is the Rydberg's constant. This is the same as Eq. (5.11) derived empirically by Rydberg to explain the hydrogen spectrum, with the data available at that time. For hydrogen, $R = R_H$.

$$\bar{\nu} = \frac{1}{\lambda} = R_H\left(\frac{1}{(n_1)^2}-\frac{1}{(n_2)^2}\right)\text{ m}^{-1}$$

This means that the energy of the electron in an atom of hydrogen is given by

$$E = \left(\frac{-Rhc}{n^2}\right)$$

The energy of the electron in any one-electron system is given by

$$E = \left(\frac{-Z^2Rhc}{n^2}\right)$$

The different series of spectral lines obtained in atomic spectra of hydrogen can be obtained by varying the values of n_i and n_f in Eq. (5.11). Thus with $n_f = 1$and $n_i = 2$, 3, 4, etc., we obtain the Lyman series of lines in the UV region. With $n_f = 2$ and $n_i = 3, 4, 5$, etc., we get the Balmer series of lines in the visible spectrum. Similarly, $n_f = 3$ and $n_i = 4, 5, 6$, etc., gives the Paschen series, $n_f = 4$ and $n_i = 5$, 6, 7, etc., gives the Brackett series, and $n_f = 6$ and $n_i = 7, 8$, 9, etc., gives the Pfund series.

The intensity of spectral lines depends upon the number of photons of the required frequency emitted and absorbed.

The various transitions which are possible between orbits of hydrogen are shown in Fig. 5.19. The orbits are

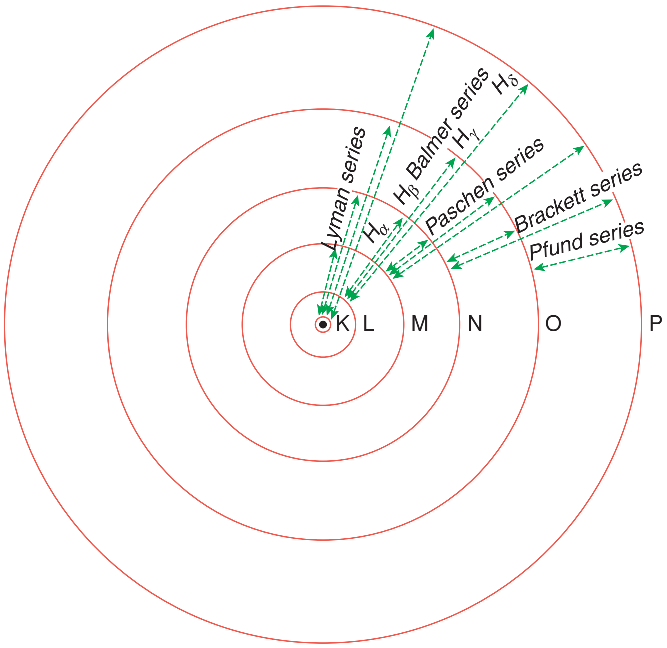


Figure 5.19 Bohr orbits of hydrogen and the various series of spectral lines.

sometimes denoted by the letters K, L, M, N, … , counting outwards from the nucleus, and they are also numbered 1, 2, 3, 4, …. This number is called the principal quantum number, which is given the symbol *n*. It is therefore possible to define which circular orbit is under consideration by specifying the principal quantum number.

> **Note:** When an electron moves from one orbit to another, it should give a single sharp line in the spectrum, corresponding precisely to the energy difference between the initial and final orbits. If the hydrogen spectrum is observed with a high resolution spectrometer, it is found that some of the lines reveal "fine structure." This means that a line is really composed of several lines close together.

Ionization Energy (Enthalpy)

Ionization enthalpy is the energy required to remove the electron from the atom in gaseous state and convert it into an ion. In terms of Bohr's theory it amounts to a transition of electron from ground state $n = 1$ to $n = \infty$ on absorption of energy equal to ionization enthalpy. It is thus possible to calculate the ionization enthalpy of hydrogen and hydrogen-like species using the formulas

$$E_n = -\frac{2.18\times10^{-18}}{n^2}\ \text{J atom}^{-1} \quad \text{(for hydrogen)}$$

$$E_n = -\frac{2.18\times10^{-18}}{n^2}Z^2\ \text{J atom}^{-1} \quad \text{(for hydrogen-like species)}$$

Solved Example 5-15

Calculate the energy of an electron in the *n*th orbit of a hydrogen atom.

Solution

The energy of a Bohr orbit is given by

$$E_n = -\frac{2\pi^2 mk^2e^4}{n^2h^2}$$

where $k = \dfrac{1}{4\pi\epsilon_0} = 8.99\times10^9\ \text{kg m}^3\text{s}^{-2}\text{C}^{-2}$ and taking $Z = 1$. We know that mass of an electron $(m) = 9.11 \times 10^{-31}$ kg and charge on electron is $(e) = 1.602 \times 10^{-19}$ C, $h = 6.626 \times 10^{-34}$ kg m^2 s^{-1}. Substituting values in the equation, we get

$$E_n = \frac{2\times(22)^2\ (9.11\times10^{-31})\,(8.99\times10^{9})^2\ (1.602\times10^{-19})^4}{(7)^2\times n^2\times(6.626\times10^{-34})^2}$$

$$= -\frac{2.18\times10^{-18}}{n^2}\ \text{J}$$

Solved Example 5-16

Calculate the distance of an electron from the nucleus in the first orbit of a hydrogen atom.

Solution

For hydrogen atom $Z = 1$, and for the first orbit $n = 1$, therefore

$$r = \frac{h^2}{4\pi^2 m_e ke^2} \qquad (1)$$

where $k = 1/(4\pi\epsilon_0) = 8.99 \times 10^9$ kg m^3 s^{-2} C^{-2}. We know that $h = 6.626 \times 10^{-34}$ J s $= 6.626 \times 10^{34}$ kg m^2 s^{-1}, mass of an electron $(m_e) = 9.11 \times 10^{-31}$ kg, charge on an electron $(e) = 1.602 \times 10^{-19}$ C.

On substituting the values into Eq. (1), we get

$$r = \frac{(6.626\times10^{-34})^2\ \text{kg}^2\ \text{m}^4\ \text{s}^{-2}}{4\times(3.14)^2(9.11\times10^{-31}\,\text{kg})(8.99\times10^{9}\ \text{kg}\,\text{m}^3\ \text{s}^{-2}\ \text{C}^{-2})} \times\frac{1}{(1.602\times10^{-19}\ \text{C})^2}$$

Therefore, $r = 5.29\times10^{-11}\ \text{m} = 0.0529\times10^{-9}\ \text{m} = 0.0529\ \text{nm}$.

Solved Example 5-17

How far from the nucleus is the electron in a hydrogen atom if it has energy of –0.850 eV.

Solution

According to Bohr's theory,

$$E_n = -\frac{Z^2}{n^2} \times 21.69 \times 10^{-19}$$

where E_n is the total energy of electron in that shell. Substituting –0.850 eV, we get

$$-\frac{Z^2}{n^2} \times 21.69 \times 10^{-19} = -0.85 \times 1.6 \times 10^{-19}$$

Substituting $n = 4$ for $Z = 1$, we get

$$r = \frac{n^2}{Z} \times 0.529 = \frac{16}{1} \times 0.529 = 8.46 \text{ Å}$$

Solved Example 5-18

Photochemical dissociation of oxygen results in the production of two oxygen atoms, one in the ground state and one in the excited state,

$$O_2 \xrightarrow{h\nu} O + O^*$$

The maximum wavelength needed for this is 174 nm. If the excitation energy O → O* is 3.15×10^{-19} J. How much energy in kJ mol^{-1} is needed for the dissociation of one mole of oxygen into normal atoms in ground state?

Solution

Energy required per molecule in the following process may be given as

$$O_2 \xrightarrow{h\nu} O + O^*$$

$$E = \frac{h \times c}{\lambda} = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{174 \times 10^{-9}} = 11.424 \times 10^{-19} \text{ J mol}^{-1}$$

The energy for O → O$^+$ is 3.15×10^{-19} joule (excitation energy). Thus, the energy $O_2 \rightarrow 2O$ will be (dissociation energy)

$$\begin{aligned} E &= 11.424 \times 10^{-19} - 3.15 \times 10^{-19} \\ &= 8.274 \times 10^{-19} \text{ J mol}^{-1} \\ &= 8.274\ 10^{-19} \times 6.023\ 10^{23} \times 10^{-3} \text{ kJ mol}^{-1} \\ &= 498.3 \text{ kJ mol}^{-1} \end{aligned}$$

Solved Example 5-19

Calculate the wavelength and energy of radiation emitted for the electronic translation from infinity to ground state of one of the hydrogen atom. Given $c = 3 \times 10^8$ m s^{-1}, $R_H = 1.09678 \times 10^7$ m^{-1}, $h = 6.6256 \times 10^{-34}$ J s^{-1}.

Solution

According to Rydberg equation, we have

$$\bar{\nu} = \frac{1}{\lambda} = RZ^2\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

where $Z = 1$, $R = 1.09678 \times 10^7$ m^{-1}, $n_1 = 1$ and $n_2 = \infty$. Therefore,

$$\frac{1}{\lambda} = 1.09678 \times 10^7 \left[\frac{1}{1} - \frac{1}{\infty}\right]$$

or $$\lambda = \frac{1}{1.09678 \times 10^7} = 0911 \times 10^{-7} = 9.11 \times 10^{-8} \text{ m}$$

The energy is given by

$$\text{Energy, } E = \frac{hc}{\lambda} = \frac{6.6256 \times 10^{-34} \times 3 \times 10^8}{9.11 \times 10^{-8}} = 2.18 \times 10^{-18} \text{ J}$$

Solved Example 5-20

The $n = 3$ energy level is of considerably greater energy than the $n = 2$ energy level. Using the Bohr model, describe how the wavelengths of light compare as an electron falls from these two energy levels to the $n = 1$ energy level.

Solution

Since these two shells are comparatively far apart in energy, transitions from these two levels to the $n = 1$ shell have comparatively different energies. Thus, the wavelengths of light from the two transitions are quite different. (The $n = 3$ to $n = 1$ transition has a shorter wavelength than the $n = 2$ to the $n = 1$ transition.)

Solved Example 5-21

The energy of the electron in the second and the third Bohr's orbits of the hydrogen atom is -5.42×10^{-12} ergs and -2.41×10^{-12} ergs, respectively. Calculate the wavelength of the emitted radiation when the electron drops from the third to the second orbit. **(IIT-JEE 1981)**

Solution

The energy of the emitted radiation is

$$\Delta E = E_3 - E_2 = \frac{hc}{\lambda} \Rightarrow -2.41\times10^{-12} - (5.42\times10^{-12}) = \frac{hc}{\lambda}$$

$$3.01\times10^{-12}\times10^{-7} = \frac{6.626\times10^{-34}\times3\times10^{8}}{\lambda}$$

or $$\lambda = \frac{6.626\times10^{-26}\times3}{3.01\times10^{-19}} = \frac{6.626\times10^{-7}\times3}{3.01}$$

$$= 6603\ \text{Å} = 6.603\times10^{-7}\ \text{m}$$

Solved Example 5-22

Calculate the wavelength in angstroms of the photon that is emitted when an electron in the Bohr orbit, $n = 2$ returns to the orbit, where $n = 1$ in the hydrogen atom. The ionization potential of the ground state hydrogen atom is 2.17×10^{-11} ergs per atom. **(IIT-JEE 1982)**

Solution

The energy of the emitted radiation is

$$\Delta E = 2.17\times10^{-18}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \Rightarrow \frac{hc}{\lambda} = 2.17\times10^{-18}\left[1 - \frac{1}{4}\right]$$

or $$\frac{6.62\times10^{-34}\times3\times10^{8}}{\lambda} = 2.17\times10^{-18}\times\frac{3}{4}$$

or $$\lambda = \frac{4\times6.62\times3\times10^{-26}}{6.51\times10^{-18}} = \frac{79.44\times10^{-26}}{6.51\times10^{-18}}$$

$$= 12.20\times10^{-8}\ \text{Å}$$

Solved Example 5-23

Calculate the wave number for the shortest wavelength transition in the Balmer series of atomic hydrogen. **(IIT-JEE 1996)**

Solution

The shortest wavelength transition in the Balmer series corresponds to the transition $n_1 = 2$ to $n_2 = \infty$.

Hence, the wave number is

$$\bar{v} = R_{\text{H}}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = (109677\ \text{cm}^{-1})\left(\frac{1}{2^2} - \frac{1}{\infty^2}\right)$$

$$= 27419.25\ \text{cm}^{-1}$$

Solved Example 5-24

Calculate the energy required to excite one liter of hydrogen gas at 1 atm and 298 K to the first excited state of atomic hydrogen. The energy for the dissociation of H–H bond is 436 kJ mol^{-1}. **(IIT-JEE 2001)**

Solution

First, we determine the number of moles of hydrogen gas,

$$n = \frac{pV}{RT} = \frac{1\times1}{0.082\times298} = 0.0409$$

The concerned reaction is $H_2 \rightarrow 2H$; $\Delta H = 436$ kJ mol^{-1}. Energy required to bring 0.0409 mol of hydrogen gas to atomic state $= 436\times0.0409 = 17.83$ kJ.

Next, we calculate the total number of hydrogen atoms in 0.0409 mol of H_2 gas

1 mol H_2 gas has 6.02×10^{23} molecules

$$0.0409 \text{ mol of } H_2 \text{ gas} = \frac{6.02\times10^{23}}{1}\times0.0409 \text{ molecules}$$

Since 1 molecule of H_2 gas has 2 hydrogen atoms, so $6.02 \times 10^{23} \times 0.0409$ molecules of H_2 gas will have $2\times6.02\times10^{23}\times0.0409 = 4.92\times10^{22}$ atoms

The energy required to excited an electron from the ground state to the next excited state is

$$E_1 = 13.6\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = 13.6\times\left(\frac{1}{1} - \frac{1}{4}\right)$$

$$= 13.6\times\frac{3}{4} = 10.2 \text{ eV} = 1.632\times10^{-21} \text{ kJ}$$

Therefore, energy required to excite 4.92×10^{22} electrons is

$$E_2 = 1.632\times10^{-21}\times4.92\times10^{22} = 8.03\times10 = 80.3 \text{ kJ}$$

Therefore total energy required, $E_{\text{total}} = 17.83 + 80.3 = 98.13$ kJ

Solved Example 5-25

What are the frequency and wavelength of a photon emitted during a transition from $n = 5$ state to the $n = 2$ state in the hydrogen atom?

Solution

Since $n_1 = 5$ and $n_2 = 2$, this transition gives rise to a spectral line in the visible region of the Balmer series. From the equation

$$\Delta E = 2.18\times10^{18}\left[\frac{1}{5^2} - \frac{1}{2^2}\right] = -4.58\times10^{-19} \text{ J}$$

We find that it is the emission energy. The frequency of the photon (taking energy in terms of magnitude) is given by

$$\nu = \frac{\Delta E}{h} = \frac{4.58\times10^{-19}}{6.626\times10^{-34}} = 6.91\times10^{14} \text{ Hz}$$

Hence, the wavelength is

$$\lambda = \frac{c}{\nu} = \frac{3.0\times10^{8} \text{ m s}^{-1}}{6.91\times10^{14} \text{ Hz}} = 0.434 \text{ nm}$$

Solved Example 5-26

Calculate the ratio of the radius of Be^{3+} ion in third energy level to that of He^+ ion in the second energy level.

Solution

From the expression $r \propto \frac{n^2}{z}$ where n is the principal shell and Z is the atomic number, we have

$$\frac{r_1}{r_2} = \left(\frac{n_1}{n_2}\right)^2\left(\frac{Z_2}{Z_1}\right)$$

Substituting $n_1 = 3$, $n_2 = 2$, $Z_1 = 4$ for Be^{3+} and $Z_2 = 2$ for He^+, we get

$$\frac{r_1}{r_2} = \left(\frac{3}{2}\right)^2\times\left(\frac{2}{4}\right) = \frac{9}{8}$$

Solved Example 5-27

According to Bohr's theory, the electronic energy of hydrogen atom in the nth Bohr's orbit is given by $E_n = (-21.76\times10^{-19})/n^2$ J. Calculate the longest wavelength of light that will be needed to remove an electron from the third Bohr orbit of the He^+ ion. **(IIT-JEE 1990)**

Solution

The energy to remove an electron from the third Bohr orbit of the He^+ ion ($Z^2 = 4$) is

$$E_{n=3} = \frac{-21.76\times10^{-19}\times4}{9} = \frac{87.04}{9}\times10^{-19} = 9.67\times10^{-19}\text{ J}$$

Now, as $\Delta E = hc/\lambda$, we have

$$\lambda = \frac{6.626\times10^{-34}\times3\times10^{8}}{9.67\times10^{-19}} = 2.0556\times10^{-7}\text{ m} = 2055 \text{ Å}$$

Solved Example 5-28

Calculate the wavelength of electron in an orbit of Be^{3+} ion having radius equal to the Bohr's radius (a_0). Also report the accelerating potential that must be imparted to an electron originally at rest to give an effective wavelength as calculated above.

Solution

In the expression, $r_n = \frac{n^2}{Z^2} a_0$, substituting $Z = 4$ and $r = a_0$, we get

$$a_0 \frac{n^2}{4^2} a_0 \quad \Rightarrow n = 2$$

Now, the ionization enthalpy is

$$E_n = -\frac{Z^2}{n^2} \times 13.6 \text{ eV} = -\frac{4^2}{2^2} \times 13.6 = -54.4 \text{ eV}$$

So, the kinetic energy $= -E_n = 54.4$ eV. Thus, the wavelength can be calculated as

$$\lambda = \frac{h}{\sqrt{2mE}} = \frac{6.626 \times 10^{-34}}{\sqrt{2 \times 9.11 \times 10^{-31} \times 54.4 \times 1.6 \times 10^{-19}}}$$
$$= 1.66 \times 10^{-10} = 1.66 \text{ Å}$$

Solved Example 5-29

Estimate the difference in energy between first and second Bohr orbits for a hydrogen atom. At what minimum atomic number, a transition from $n = 2$ to $n = 1$ energy level would result in the emission of X-rays with $\lambda = 3.0 \times 10^{-6}$ m? Which hydrogen atom-like species does this atomic number correspond to? **(IIT-JEE 1993)**

Solution

From the expression $\Delta E = E_1 - E_1 = \frac{hc}{\lambda}$, we have

$$-2.18 \times 10^{-18} \times Z^2 \left[\frac{1}{(1)^2} - \frac{1}{(2)^2} \right] = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{3 \times 10^{-6}}$$

$$-2.18 \times 10^{-18} \times Z^2 \times \frac{3}{4} = 6.626 \times 10^{-18}$$

or $$Z^2 = \frac{6.626 \times 10^{-18} \times 4}{2.18 \times 10^{-18} \times 3} = 4 \quad \Rightarrow Z = 2$$

Thus, the species is He^+ with $Z = 2$.

Line Spectra of Hydrogen

If a discharge is passed through a glass tube containing hydrogen gas (H_2) at a low pressure, some hydrogen atoms (H) are formed, which emit light (pink–violet) in the visible region. This light can be studied with a spectrometer, and is found to comprise a series of lines of different wavelengths. Four lines can be seen by eye, but many more are observed photographically in the ultraviolet region. The lines become increasingly close together as the wavelength (λ) decreases, until the continuum is reached.

Note: In spectroscopy, waves are generally described as wave number $\bar{\nu}$ where $\bar{\nu} = 1/\lambda$ m^{-1}. Wavelengths, in meters, are related to the frequency, ν, in Hertz (cycles per second) by the equation

$$\nu = \frac{c}{\lambda}$$

where c is the velocity of light (3×10^8 m s^{-1}).

In 1885, Balmer showed that the wave number $\bar{\nu}$ of any line in the visible spectrum of atomic hydrogen could be given by the simple empirical formula:

$$\bar{\nu} = R_H \left(\frac{1}{2^2} - \frac{1}{n^2} \right)$$

where R_H is the Rydberg constant and n has the values 3, 4, 5, …; thus giving a series of lines. This is known as the **Balmer formula**. The series of lines given by this formula is called the Balmer series which appear only in the visible region of the electromagnetic spectrum. Rydberg, a Swedish physicist, showed that the lines can be given by the following formula:

$$\bar{\nu} = 109677\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)\text{cm}^{-1} \qquad (5.12)$$

where $n_1 = 1, 2, \ldots$ and $n_2 = n_1 + 1, n_1 + 2, \ldots$. The value of Rydbverg constant is 109677 cm^{-1}. Apart from Balmer series, several other series of lines may be observed in different regions of the spectrum (Table 5.2) and Fig. 5.20.

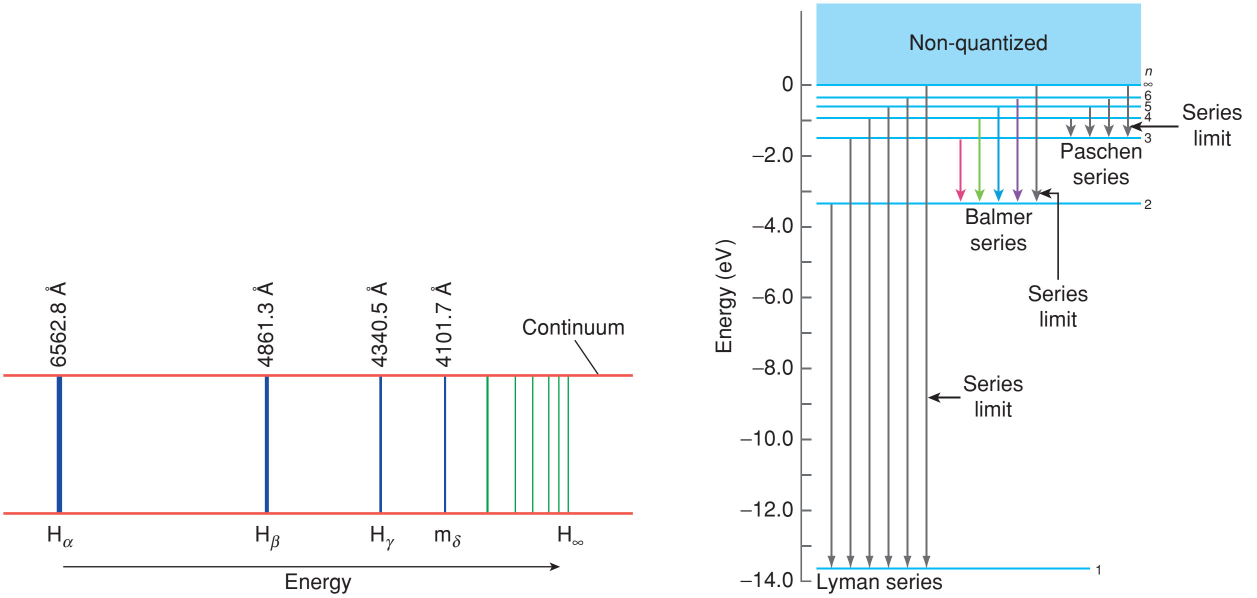


Figure 5.20 Spectrum of hydrogen.

Table 5.2 Spectral series found in atomic hydrogen

Series	Lyman series	Balmer series	Paschen series	Brackett series	Pfund series	Humphry series
Region of Spectrum	Ultraviolet	Visible/ ultraviolet	Infrared	Infrared	Infrared	Infrared

Similar equations were found to hold for the lines in the other series in the hydrogen spectrum.

$$\text{Lyman } \bar{\nu} = R_H\left(\frac{1}{1^2} - \frac{1}{n^2}\right) \quad n = 2, 3, 4, 5,. \qquad \text{Balmer } \bar{\nu} = R_H\left(\frac{1}{2^2} - \frac{1}{n^2}\right) \quad n = 3, 4, 5, 6,.$$

$$\text{Paschen } \bar{\nu} = R_H\left(\frac{1}{3^2} - \frac{1}{n^2}\right) \quad n = 4, 5, 6, 7,. \qquad \text{Brackett } \bar{\nu} = R_H\left(\frac{1}{4^2} - \frac{1}{n^2}\right) \quad n = 5, 6, 7, 8,. \qquad (5.12)$$

$$\text{Pfund } \bar{\nu} = R_H\left(\frac{1}{5^2} - \frac{1}{n^2}\right) \quad n = 6, 7, 8, 9,.$$

Total Number of Spectral Lines

Consider the case in which we have a lot of atoms and we want to calculate the total number of spectral lines possible. From Fig. 5.21, we have that the following transitions will be possible 5→1, 5→2, 5→3, 5→4, 4→1, 4→2, 4→3, 3→2, 3→1, 2→1, that is, 10 spectral lines

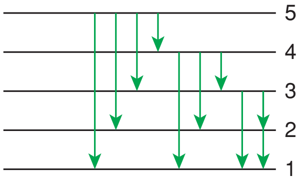


Figure 5.21 Number of spectral lines.

If n_1 and n_2 are the two energy levels between which the transition is made, then maximum number of spectral lines between them is given by

$$\frac{\Delta n(\Delta n+1)}{2}$$

where $\Delta n = n_2 - n_1$. For example, in the above case $\Delta n = 5-1=4$

Therefore, maximum number of spectral lines $= \frac{4(4+1)}{2} = 10$

Solved Example 5-30

The wavelength corresponding to maximum energy for hydrogen is 91.2 nm. Find the corresponding wavelength for He$^+$ ion. **(IIT-JEE 2003)**

Solution

For hydrogen atom

$$\frac{1}{\lambda_H} = R_H Z_H^2 \left[\frac{1}{1^2} - \frac{1}{\infty^2}\right]$$

$$\frac{1}{\lambda_H} = R_H Z_H^2 \quad (1)$$

For He$^+$ ion

$$\frac{1}{\lambda_{He}} = R_{He} \times Z_{He}^2 \quad (2)$$

Dividing Eq. (1) by Eq. (2), we get

$$\frac{\lambda_{He^+}}{\lambda_H} = \frac{R_H\, Z_H^2}{R_{He^+}\, Z_{He^+}^2}$$

Since $R_H = R_{He^+}$, we have

$$\frac{\lambda_{He^+}}{\lambda_H} = \frac{Z_H^2}{Z_{He^+}^2} = \frac{1}{4} \quad \Rightarrow \lambda_{He^+} = \frac{\lambda_H}{4} = \frac{91.2}{4} = 22.8 \text{ nm}$$

Solved Example 5-31

Wavelength of high energy transition of hydrogen atoms is 91.2 nm. Calculate the corresponding wavelength of He atoms. **(IIT-JEE 2003)**

Solution

For maximum energy, $n_1 = 1$ and $n_2 = \infty$. Hence, we have

$$\frac{1}{\lambda} = R_H Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Since R_H is a constant and transition remains the same,

$$\frac{1}{\lambda} \propto Z^2 \Rightarrow \frac{\lambda_{He}}{\lambda_H} = \frac{Z_H^2}{Z_{He}^2} = \frac{1}{4}$$

Hence, $\lambda_{He} = \frac{1}{4} \times 91.2 = 22.8$ nm

Limitations of Bohr's Model

By calculating the energy changes that occur between energy levels, Bohr was able to account for the Rydberg equation and, therefore, for the atomic spectrum of hydrogen. However, the theory was not able to explain quantitatively the spectra of atoms with more than one electron, and all attempts to modify the theory to make it work met with failure. Some important deficiencies of Bohr's theory are listed as follows:

1. It accounts for the line spectra of only one-electron systems such as H, He^+ and Li^{2+}.
2. Each of the four lines of the hydrogen spectrum observed by Balmer, when viewed through a high-resolution spectrometer, is found to be made up of six different lines. Bohr's theory does not explain this.
3. It assumes that electrons revolved round the nucleus in circular orbits. Sommerfeld explained the splitting of the spectral lines of hydrogen by assuming that some electron orbits were elliptical.
4. It does not explain the splitting of spectral lines by magnetic fields (Zeeman effect) and by electric fields (Stark effect).
5. According to this theory, the total energy of an electron is the sum of its potential and kinetic energies. It is now known that electrons spin on their own axis. The energy of the spin is not taken into account in Bohr's theory.
6. Bohr assumes that the angular momentum of an electron in an atom of hydrogen is an integral multiple of $h/2\pi$ but his theory does not explain the reason for this assumption.
7. Using this theory, we are able to find the position of an electron and its velocity in an atom of hydrogen. But according to Heisenberg's uncertainty principle, it is impossible to know both the position and momentum of a fast-moving electron accurately.
8. It does not take into account the wave nature of the electron.

Bohr–Sommerfeld Model

Bohr's model was extended by Sommerfeld to study the line spectrum of one-electron systems. Using a high resolving power spectroscope, it was found that a line is a collection of more than one fine line of similar wavelength, resulting in a fine spectrum. Some of the important features of the model were

1. It described the orbits containing electrons revolving around the nucleus to be elliptical instead of being circular with definite energy levels.
2. It described the atom using two quantum numbers instead of one, that is, n and k where k is called azimuthal quantum number. It is equal to $1, 2,\ldots n$ but $k \neq 0$. Thus, when a transition of electron takes place from a higher level to a lower one, it would be differ from that proposed by Bohr because there could be more than one values of k. Thus, the reason from fine spectrum could be explained.
3. It stated that the angular momentum of electron in closed elliptical paths is quantized, that is $L_k = k(h/2\pi)$
4. The relation between n and k gives an estimate of possible number of subshells contained in a shell. The ratio of n to k is numerically equal to the ratio of the length of major axis to that of minor axis. On increasing k, the path becomes more eccentric, whereas if $n/k = 1$, then the path is circular.

In spite of the enhanced features, there were certain limitations to Sommerfeld theory. These are as follows:

1. It was restricted to one-electron systems only, and could not explain the spectrum and electron–electron repulsions of polyelectron systems.
2. It was unable to explain the de Broglie equation, even though it indicated that momentum in closed elliptical paths is quantized.

5.11 | PHOTOELECTRIC EFFECT

Photoelectric effect is the phenomenon in which electrons are emitted from a metal surface when radiation of sufficient energy falls on it. Metals such as sodium, lithium and potassium show photoelectric effect with visible light, whereas metals like zinc, magnesium, and cadmium show photoelectric effect with ultraviolet light.

The phenomenon of photoelectric emission was discovered in 1887 by Heinrich Hertz (1857–1894) during his electromagnetic wave experiment. Hertz found that high voltage sparks across a detector loop were enhanced when an emitter plate was illuminated by ultraviolet light from an arc lamp. This was explained as follows: When the emitter plate was illuminated by ultraviolet light, some electrons near the surface of the metallic emitter plate absorb energy from the ultraviolet rays. This enables them to overcome the force of attraction due to positive ions in the material of the emitter and finally escape from the emitter surface into the surrounding space, hence enhancing the high voltage sparks across the detector. Because the electrons are ejected with the aid of light, they are called **photoelectrons**.

In another experiment, a negatively charged zinc plate was connected to an electroscope. It was found that the zinc plate lost its charge when it was illuminated by ultraviolet light. The uncharged zinc plate became positively charged when it was irradiated by ultraviolet light. It was concluded that the negatively charged particles were emitted from the zinc plate under the action of ultraviolet light. These observations were formulated as the **laws of photoelectric effect**.

1. The electrons are ejected from the surface as soon as the surface was irradiated by the beam of light.
2. The number of electrons emitted from the surface is proportional to the intensity of the incident beam.
3. Electrons could be made to leave a metal's surface only if the frequency of the incident radiation was above some minimum value, which was named the **threshold frequency** (ν_0). This threshold frequency differs for different metals, depending on how tightly the metal atom holds onto electrons.
4. Above the threshold frequency ($\nu > \nu_0$), the ejected electrons come out with certain kinetic energy. The kinetic energy of the emitted electron increases with increasing frequency of the light. In his photoelectric theory, Einstein proposed that light of frequency ν could be regarded as a collection of discrete packets of energy (photons), each packet containing an amount of energy E given by $E = h\nu$ where h is Planck's constant.

Einstein explained the photoelectric effect thus: *An electron absorbs a quantum of energy* (nh) *from light and if the energy absorbed is greater than the minimum energy* ($h\nu_0$) *required by an electron to escape from the metal surface (known as work function* W_0*), then the electron is ejected from the metal surface with some kinetic energy.* Einstein summed up the results of the photoelectric experiments in the equation:

$$h\nu = \text{K.E.} + h\nu_0 = \frac{1}{2}mv^2 + h\nu_0$$

$$\text{K.E.} = h\nu - W$$

where K.E. is the kinetic energy of the electron that is emitted, $h\nu$ is the energy of the photon of frequency ν and $h\nu_0$ is the minimum energy needed to eject the electron from the metal's surface.

Solved Example 5-32

Calculate both the energy of a single photon of red light with a wavelength of 700.0 nm and the energy of a mole of such photons.

Solution

The red light with a wavelength of 700.0 nm has a frequency of 4.283×10^{14} s^{-1}. This should be calculated and shown.

$$\nu = \frac{c}{\lambda} = \frac{3.0\times10^8}{700\times10^{-9}} = 4.286\times10^{14}\ \text{s}^{-1}$$

Substituting this frequency into the Planck–Einstein equation gives the following result in units of joules (J).

$$E = h\nu = (6.626\times10^{-34}\ \text{J s})(4.283\times10^{14}\ \text{s}^{-1})$$
$$= 2.838\times10^{-19}\ \text{J}$$

A mole of the photons has 170.9 kJ of energy.

$$\frac{2.838\times10^{-19}\ \text{J}}{1\ \text{photon}} \times \frac{6.022\times10^{23}\ \text{photons}}{1\ \text{mol}} = 1.709\times10^{5}\ \text{J mol}^{-1}$$
$$= 170.9\ \text{kJ mol}^{-1}$$

Solved Example 5-33

In a photoelectric experiment, the collector plate is at 2.0 V with respect to emitter plate made of copper (work function 4.5 eV). The emitter is illuminated by a source of monochromatic light of wavelength 200 nm. Find the minimum and maximum kinetic energy of photoelectrons reaching the collector.

Solution

Since plate potentials = 2 V, minimum K.E. will be 2 eV. For maximum K.E., use the following relation:

$$\text{Absorbed energy} = \text{Threshold energy} + \text{K.E.}$$

$$\frac{hc}{\lambda} = 4.5\times 1.6\times 10^{-19} + \text{K.E.}$$

$$\frac{6.626\times 10^{-34}\times 3\times 10^{8}}{200\times 10^{-9}} = 4.5\times 1.6\times 10^{-19} + \text{K.E.}$$

$$\text{K.E.} = 2.739\times 10^{-19}\ \text{J} = 1.7\ \text{eV}$$

Hence, the maximum K.E. = 2 + 1.7 = 3.7 eV.

Solved Example 5-34

A 100 W bulb emits monochromatic light of wavelength 400 nm. Calculate the number of photons emitted per second by the bulb.

Solution

Given that power of the bulb = 100 watt = 100 J s^{-1}. We know that

Energy of one photon

$$E = nh\nu$$

$$= \frac{6.626\times 10^{-34}\ \text{J s}\times 3\times 10^{8}\ \text{m s}^{-1}}{400\times 10^{-9}\ \text{m}}$$

$$= 4.969\times 10^{-19}\ \text{J}$$

$$\text{Number of photons emitted} = \frac{100\ \text{J}\ s^{-1}}{4.969\times 10^{-19}\ \text{J}}$$

$$= 2.012\times 10^{20}\ \text{s}^{-1}$$

Solved Example 5-35

The threshold frequency ν_0 for a metal is 7.0 × 10^{14} s^{-1}. Calculate the kinetic energy of an electron emitted when radiation of frequency $\nu = 1.0\times 10^{15}\ \text{s}^{-1}$ hits the metal.

Solution

According to Einstein's equation, we have

$$\text{K.E.} = \frac{1}{2}m_e v^2 = h(\nu - \nu_0)$$

$$= (6.626\times 10^{-34}\ \text{J s})(10.0\times 10^{14}\ \text{s}^{-1} - 7.0\times 10^{14}\ \text{s}^{-1})$$

$$= (6.626\times 10^{-34}\ \text{J s})(3.0\times 10^{14}\ \text{s}^{-1})$$

$$= -1.988\times 10^{-19}\ \text{J}$$

Solved Example 5-36

A certain metal was irradiated with light of frequency 3.2 × 10^{16} Hz. The photoelectrons emitted had twice the kinetic energy as did photoelectrons emitted when the same metal was irradiated with light of frequency 2×10^{16} Hz. Calculate the threshold frequency for the metal.

Solution

We have the relation

$$\text{K.E.} = h\nu - h\nu_0 \quad \text{or} \quad \nu - \nu_0 = \frac{\text{K.E.}}{h}$$

Given that $(\text{K.E.})_2 = 2(\text{K.E.})_1$. Therefore, we have

$$\frac{\nu_2 - \nu_0}{\nu_1 - \nu_0} = \frac{(\text{K.E.})_2/h}{(\text{K.E.})_1/h} = 2$$

or $$\nu_2 - \nu_0 = 2\nu_1 - 2\nu_0$$

Hence, $$\nu_0 = 2\nu_1 - \nu_2$$

$$= (4\times 10^{16}) - (3.2\times 10^{16})$$

$$= 8\times 10^{15}\ \text{Hz}$$

Detailed Analysis of Photoelectric Effect

1. **Stopping potential (V_s):** It is defined as the potential necessary to stop the electron having the maximum K.E. which has been emitted in photoelectric effect.

$$eV_s = (\text{K.E.})_{\max}$$

2. **Accelerating Potential Voltage (V):** If accelerating voltage is provided to an emitted electron, then it will further increase the K.E. of the emitted electron. For example, if accelerating voltage V_1 is applied, then the emitted electron will have minimum kinetic energy eV_1 and maximum kinetic energy = $(\text{K.E.})_{\max} + eV_1$.

Note: In photoelectric effect, the ejected photoelectrons can have any K.E. from 0 to $(\text{K.E.})_{\max}$.

3. The $(\text{K.E.})_{\max}$ of the ejected photoelectron is directly proportional to frequency v of the radiation. It is independent of the intensity of the radiation (Fig. 5.22).

$$hv = hv_0 + (\text{K.E.})_{\max}$$

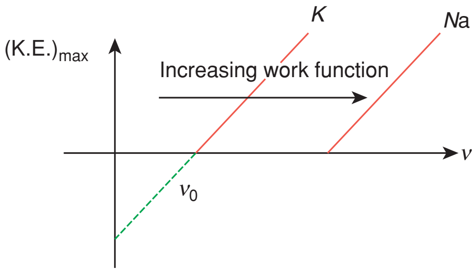


Figure 5.22 Kinetic energy of emitted electron as a function of frequency of incident radiation.

4. The magnitude of photocurrent is directly proportional to intensity of radiation (assuming same metal on which different intensities of photons are radiated). As each photon can eject maximum of one photoelectron, as intensity increases, the number of photons increases and thus, number of photoelectrons ejected increases (Fig. 5.23). As a result, photocurrent increases.

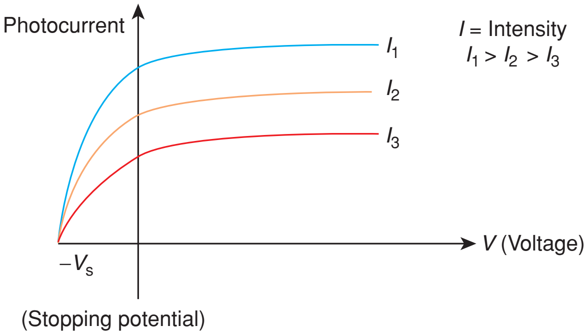


Figure 5.23 Photocurrent as a function of intensity of incident radiation (assuming same metal).

5.12 | DUAL NATURE OF MATTER

The planetary theory of atomic structure put forward by Rutherford and Bohr describes the atom as a central nucleus surrounded by electrons in certain orbits. The electron is thus considered as a particle. In the 1920s, it was shown that moving particles such as electrons behaved in some ways as waves. The two important developments in that regard were dual behavior of matter and Heisenberg uncertainty principle.

de Broglie Equation

When bound inside an atom, electrons behave not like solid particles, but instead like waves. This idea was proposed in 1924 by a young French graduate student, Louis de Broglie. The matter waves, like the light waves are characterized by their wavelengths and their frequencies. For matter waves $E = mc^2$ and for light waves $E = hc/\lambda$. Therefore, $\lambda = h/mc$· The general form of equation is

$$\lambda = \frac{h}{mv} = \frac{h}{p}$$

where h is Planck's constant, m is the particle's mass, v is its velocity and p is the momentum.

When kinetic energy is given,

$$\text{K.E.} = \frac{1}{2}mv^2 = \frac{p^2}{2m}.$$

These relations allow us to connect a wave property, wavelength, with particle properties, mass and velocity. We may describe the electron either as a particle or a wave, and the de Broglie relationship provides a link between the two descriptions. Electrons are no longer assumed to be moving in circular stationary orbits as proposed by Bohr. According to de Broglie, electrons move in the form of waves. The circumference of the nth orbit in a one-electron system is equal to n (the de Broglie wavelength of the electron). Just as in case of electromagnetic radiation, some properties of electrons can be explained on the basis of wave nature and the others on the basis of particle nature. The distinguishing features of electromagnetic waves and matter waves are shown in Table 5.3.

Table 5.3 Electromagnetic waves vs. matter waves

Electromagnetic waves	Matter waves
They are associated with electrical and magnetic fields perpendicular to each other and to the direction of propagation.	They may not be associated with electrical and magnetic fields.
They travel with the same speed.	They travel with different speeds.
Their velocity is that of light.	Their velocity is generally less than that of light.
They do not require medium for propagation.	They require a medium for propagation (cannot travel through vacuum).
They can be radiated into space or emitted.	They cannot be radiated into space or emitted by particles.
Their wavelength is generally large and given by the relation $\lambda = \frac{c}{v}$	Their wavelengths are generally shorter and given by de Broglie's equation $\lambda = \frac{h}{mv}$

Experimental Evidence for Wave Nature of Electrons

The first experimental proof for wave nature of electrons demonstrated by American physicists Davisson and Germer. The principle involved was that since the wavelength of an electron is of the order of spacing of atoms of a crystal, a beam of electrons shows diffraction effects when incident on a crystal.

In the experimental set up, electrons from a hot tungsten cathode are accelerated by potential difference V between the cathode (C) and the anode (A). A narrow hole in the anode renders the electrons into a fine beam and allows it to fall on a nickel crystal. The electrons are scattered by the atoms in the crystal in all direction and pattern of the scattered beam is captured by a detector (Fig. 5.24).

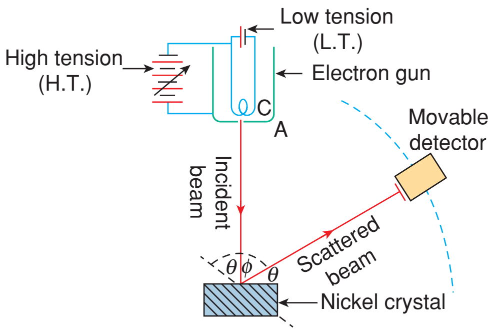


Figure 5.24 Davisson and Germer experiment.

Davisson and Germer made the following modifications in de Broglie's equation: If the charged particle (electron) is accelerated with a potential of V, then kinetic energy is given by:

$$\frac{1}{2}mv^2 = eV \Rightarrow m^2v^2 = 2eVm \Rightarrow mv = \sqrt{2eVm}$$

Then from de Broglie's relation, we have

$$\lambda = \frac{h}{mv} = \frac{h}{\sqrt{2eVm}} = \frac{1.22\ \text{nm}}{\sqrt{V}} \quad \text{where } V \text{ is in Volts.}$$

For any charged particle of charge q,

$$\text{K.E.} = \frac{1}{2}mv^2 = qV$$

$$\lambda = \frac{h}{\sqrt{2qVm}}$$

The expression for de Broglie wavelength associated with various particles is given in Table 5.4.

Table 5.4 de Broglie wavelengths for subatomic particles

Particle	Electron	Proton	Neutron	α-particle	Gas molecule
de Broglie wavelength	$\lambda = \frac{1.227}{\sqrt{V}}$ nm	$\lambda = \frac{0.0286}{\sqrt{V}}$ nm	$\lambda = \frac{0.0286}{\sqrt{V}}$ nm	$\lambda = \frac{0.0101}{\sqrt{V}}$ nm	$\lambda = \frac{h}{m \times v_{\text{rms}}} = \frac{h}{\sqrt{3mkT}}$

Solved Example 5-37

Calculate the wavelength of a particle of mass 3.1×10^{-31} kg that is moving with a speed of 2.21×10^7 m s^{-1}. (Use $h = 6.626 \times 10^{-34}$ J s)

Solution

The wavelength of the particle can be computed using de Broglie's equation $\lambda = h/mv$. Given that mass of the particle $(m) = 3.1 \times 10^{-31}$ kg, velocity of particle $= 2.21 \times 10^7$ m s^{-1}, $h = 6.626 \times 10^{-34}$ J s $= 6.626 \times 10^{-34}$ kg m^2 s^{-1}. Substituting values in equation, we get

$$\lambda = \frac{6.626 \times 10^{-34}\,\text{kg}\,\text{m}^2\,\text{s}^{-1}}{(3.1 \times 10^{-31}\,\text{kg}) \times (2.21 \times 10^7\,\text{m}\,\text{s}^{-1})} = 9.67 \times 10^{-11}\,\text{m}$$

Solved Example 5-38

Show that de Broglie wavelength of electrons accelerated V volt is very nearly given by λ (in Å) $= (150/V)^{1/2}$.

Solution

The wavelength is given by

$$\lambda = \sqrt{\frac{h}{2eVm}}$$

as $\lambda = h/mv$ and K.E. $= eV = (1/2)mv^2$. Now,

$$\lambda = \left[\frac{h^2}{2e\ Vm} \times 10^{20}\right]^{1/2}$$

$$\text{Å} = \left[\frac{(6.626 \times 10^{-34})^2 \times 10^{20}}{2 \times 1.6 \times 10^{-19} \times V \times 9.1 \times 10^{-31}}\right]^{1/2} = \left[\frac{150}{V}\right]^{1/2}$$

Solved Example 5-39

Find out the number of waves made by a Bohr electron in one complete revolution in its third orbit.

(IIT-JEE 1994)

Solution

The number of waves that a Bohr electron makes in an orbit is in fact its principle quantum number. Now, using Bohr's postulate of angular momentum in the third orbit, we get

$$mvr = n\frac{h}{2\pi} \quad \text{where } n = 3 \text{ for third orbit.}$$

According to de Broglie's equation, $\lambda = h/mv$. Substituting this in the above expression, we get

$$\left(\frac{h}{\lambda}\right)\times r = 3\left(\frac{h}{2\pi}\right) \Rightarrow 3\lambda = 2\pi r$$

Thus, we have that the circumference of the third orbit is equal to three times the wavelength of the electron; or in other words, the number of waves made by a Bohr electron in one complete revolution in its third orbit is three.

Solved Example 5-40

A ball of mass 100 g is moving with 100 m s^{-1}. Find its wavelength. **(IIT-JEE 2004)**

Solution

The wavelength is

$$\lambda = \frac{h}{mv} = \frac{6.627\times10^{-34}}{0.1\times100}$$
$$= 6.627\times10^{-35}\text{ m} = 6.627\times10^{-25}\text{ Å}$$

Solved Example 5-41

An electron beam can undergo diffraction by crystals. Through what potential should a beam of electrons be accelerated so that its wavelength becomes equal to 1.54 Å. **(IIT-JEE 1997)**

Solution

From the expressions $\frac{1}{2}mv^2 = eV$ and $\lambda = \frac{h}{mv}$, we get

$$\frac{1}{2}m\frac{h^2}{m^2\lambda^2}\text{ eV} \quad \Rightarrow V = \frac{1}{2}\frac{h^2}{m\lambda^2 e}$$

Substituting values, we get

$$V = \frac{1\times(6.62\times10^{-34})^2}{2\times9.108\times10^{-31}\times(1.54\times10^{-10})^2\times1.602\times10^{-19}}$$
$$= 63.3\text{ V}$$

5.13 | HEISENBERG'S UNCERTAINTY PRINCIPLE

Calculations on the Bohr model of an atom require precise information about the position of an electron and its velocity. **According to Heisenberg's uncertainty principle, it is difficult to measure both quantities accurately at the same time**. An electron is too small to see and may only be observed if perturbed. For example, we could hit the electron with another particle such as a photon or an electron, or we could apply an electric or magnetic force to the electron. This will inevitably change the position of the electron, or its velocity and direction. Heisenberg stated that the more precisely we can define the position of an electron, the less certainly we are able to define its velocity, and vice versa. If Δx is the uncertainty in defining the position and Δp_x (or Δv_x) the uncertainty in the momentum (or velocity), the uncertainty principle may be expressed mathematically as:

$$\Delta x\cdot\Delta p_x \ge \frac{h}{4\pi}$$

or

$$\Delta x\cdot\Delta(mv_x) \ge \frac{h}{4\pi} \quad \Rightarrow \Delta x\cdot\Delta v_x \ge \frac{h}{4\pi m}$$

where h = Planck's constant = 6.626×10^{-34} J s.

Note: When visible light falls on a macroscopic object, the photons of the incident light are scattered by the object and the reflected light enters our eye. We are thus able to see the object, determine its position and estimate its velocity. The position and velocity of the macroscopic object does not undergo any distinct change on impact of radiation (photon of energy). In contrast, microscopic objects, undergoes considerable change in its path and velocity (or momentum) on being struck by a photon of radiation. Thus, it is not possible to simultaneously determine the position and velocity of microscopic object like an electron.

Significance of Uncertainty Principle

1. The uncertainty principle limits the precision with which two complementary properties – position and momentum – of a subatomic particle can be measured. The principle has been expanded to include energy and position, angular position and angular momentum, and other pairs of variables that cannot be simultaneously known.
2. It also leads to the conclusion that the properties of a subatomic particle observed are not independent of the observer and can take a range of values.
3. Using Bohr's atomic theory, we could calculate the radius of a one-electron system (such as H, He^+ and Li^{2+}) and the velocity of the electron in orbit. But according to Heisenberg's uncertainty principle, it is not possible to know the position or the velocity of an electron with any degree of accuracy. Therefore, we can only describe the probability of finding an electron in a given volume rather than its exact position. In diagrams drawn to show the position of electrons, their position at different instances of time is marked as dots. The radius of an atom of hydrogen is arbitrarily taken to be the radius of the sphere within which the electron is found 90% of the time.
4. For objects of large mass, the uncertainty in the position (Δx) and the uncertainty in the velocity (Δv) are insignificant because the value of $h/4\pi$ is very small and is equal to 5.273×10^{-35} J s and its mass is very large compared to the value of $h/4\pi$.
5. Heisenberg's principle becomes significant in case of microscopic objects like an electron. The mass of an electron is 9.11×10^{-31} kg, then according to Heisenberg's principle

   $$\Delta x \cdot \Delta v_x \geq \frac{h}{4\pi m}$$

   Substituting values, we get

   $$\Delta x \cdot \Delta v_x \geq \frac{6.626 \times 10^{-34}}{4 \times 3.14 \times 9.11 \times 10^{-31}} = 5.79 \times 10^{-5}\ \text{m}^2\ \text{s}^{-1}$$

   If we try to find the exact location of the electron, say to an uncertainty of 10^{-9} m, then the uncertainty in its velocity will be of the order of

   $$\Delta x \cdot \Delta v_x \geq \frac{0.579 \times 10^{-4}\ \text{m}^2\ \text{s}^{-1}}{10^{-9}\ \text{m}} = 5.79 \times 10^{4}\ \text{m s}^{-1}$$

   This shows that it is difficult to justify the classical picture of atom based on Bohr's theory that gives exact position and velocity of the electron in a Bohr orbit.

Note: Heisenberg's uncertainty principle in terms of time and energy. For photon $E = mc^2 = (mc)(c) = pc$.

Therefore,

$$p = \frac{E}{c} \text{ or } \Delta p = \frac{\Delta E}{c}$$

$$\Delta x \times \Delta p \geq \frac{h}{4\pi}$$

$$\left(\frac{\Delta x}{c}\right) \times \Delta E \geq \frac{h}{4\pi} \Rightarrow \Delta t \times \Delta E \geq \frac{h}{4\pi}$$

Solved Example 5-42

The uncertainty for the calculation of radius of the first Bohr orbit is 2% for the hydrogen atom. What will be the uncertainty in velocity of electron in the first Bohr orbit. (Given that $h = 6.626 \times 10^{-34}$ J s and $m = 9.1 \times 10^{-31}$ kg.)

Solution

We know that $r = 0.529 \times 10^{-10}$ m. If uncertainty is 2%, we get

$$\Delta x = 0.529 \times 10^{-10} \times \frac{2}{100} = 1.06 \times 10^{-12}\ \text{m}$$

From Heisenberg's uncertainty principle, we have

$$\Delta x \cdot m\Delta v \geq \frac{h}{4\pi}$$

where Δx is the uncertainty in position and Δv is the uncertainty in velocity. Thus, we have

$$\Delta v \geq \frac{6.626 \times 10^{-34}}{4 \times 3.14 \times 9.1 \times 10^{-31} \times 1.06 \times 10^{-12}}$$

or $$\Delta v \geq 5.47 \times 10^{7}\ \text{m s}^{-1}$$

Solved Example 5-43

A baseball (m = 200 g) is moving with velocity of 3000 cm s^{-1}. If its position is located with an uncertainty of 500 nm, what will be the uncertainty in velocity?

Solution

From Heisenberg's principle, we have $\Delta x \times \Delta p = h/4\pi \Rightarrow \Delta x \times \Delta v = h/4\pi m$. So,

$$\Delta v = \frac{6.6 \times 10^{-34}}{500 \times 10^{-9} \times 4 \times 3.14 \times 200 \times 10^{-3}} = 0.52 \times 10^{-27}\ \text{m s}^{-1}$$

Solved Example 5-44

What is the maximum precision with which the momentum of an electron can be known if the uncertainty in the position of electron is ± 0.001 Å? Will there be any problem in describing the momentum if it has a value $h/2\pi a_0$ where a_0 is Bohr's radius of first orbit, that is, 0.529 Å.

Solution

From Heisenberg's principle, we have $\Delta x \times \Delta p = h/4\pi$. Given that $\Delta x = \pm 0.001$ Å $= 10^{-13}$ m. The uncertainty in momentum is

$$\Delta p = \frac{6.625 \times 10^{-34}}{4 \times 3.14 \times 10^{-13}} = 5.27 \times 10^{-22}\ \text{kg m s}^{-1}$$

Now, the given momentum is

$$\frac{h}{2\pi a_0} = \frac{6.626 \times 10^{-34}}{2 \times 3.14 \times 0.525 \times 10^{-10}} = 2 \times 10^{-24}\ \text{N s}$$

The uncertainty in momentum seems to be about $\left(\frac{5.27 \times 10^{-22}}{2 \times 10^{-24}}\right) = 263.5$ times as large as the momentum itself.

5.14 | NUMBER OF WAVES MADE BY THE ELECTRON

Let the number of waves made be n_1, then

$$2\pi r = n_1 \lambda \tag{5.13}$$

Also, $$\lambda = \frac{h}{mv} \quad \text{(By de Broglie's equation)} \tag{5.14}$$

and

$$mvr = \frac{nh}{2\pi} \tag{5.15}$$

where n is principal quantum number.

From Eq. (5.13), (5.14) and (5.15), we get

$$2\pi\left(\frac{nh}{2\pi\, mv}\right) = n_1\left(\frac{h}{mv}\right)$$

Therefore,

$$n = n_1$$

Thus, the number of waves made by an electron is equal to its principal quantum number.

5.15 | QUANTUM MECHANICAL MODEL OF ATOM

Quantum mechanical theory of atomic structure was proposed to overcome the theoretical limitations in predicting the exact position of an electron at a particular instant. This theory of atomic structure is based on the wave–particle duality of matter. It is insignificant for macroscopic objects because when applied to such objects, it yields the same results as those obtained with principles of classical physics.

In quantum mechanics, the concept of an electron following a definite orbit, where its position and velocity are known exactly, is replaced by the probability of finding an electron in a particular position, or in a particular volume of space. Postulates of quantum mechanics were developed independently by Heisenberg and Schrödinger. However, the fundamental equation of wave mechanics is the Schrödinger wave equation which provides a satisfactory description of an atom in these terms of duality of wave and particle.

For a system, such as an atom, whose energy does not change with time, the Schrödinger equation is given by

$$\hat{H}\psi = E\psi$$

Here $\hat{H}$ is a mathematical operator called Hamiltonian which is constructed based on the total energy of the system. Schrödinger took into consideration all the energies associated with the system, that is, the kinetic energy of all subatomic particles and potential energy of attraction between electrons and nuclei and that of repulsion among nuclei and electrons. Solutions to the wave equation are called **wave functions** and given by the symbol ψ. The solution gives the probability of finding an electron at a point in space whose coordinates are x, y and z is $\psi^2(x, y, z)$ and the energy associated with it.

For a standing wave (such as a vibrating string) of wavelength λ, whose amplitude at any point along x may be described by a function $f(x)$, it can be shown that:

$$\frac{\mathrm{d}^2 f(x)}{\mathrm{d}x^2} = -\frac{4\pi^2}{\lambda_2} f(x)$$

If an electron is considered as a wave which moves in only one dimension then:

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = -\frac{4\pi^2}{\lambda^2}\psi$$

An electron may move in three directions x, y and z so this becomes

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} = -\frac{4\pi^2}{\lambda^2}\psi$$

Using the symbol ∇ instead of the three partial differentials, this is shortened to

$$\nabla^2\psi = -\frac{4\pi^2}{\lambda^2}\psi$$

The de Broglie relationship states that

$$\lambda = \frac{h}{mv}$$

where h is Planck's constant, m is the mass of an electron and v its velocity. Now,

$$\nabla^2\psi = -\frac{4\pi^2 m^2 v^2}{h^2}\psi$$

or
$$\nabla^2\psi + \frac{4\pi^2 m^2 v^2}{h^2}\psi = 0 \tag{5.16}$$

However, the total energy of the system E is made up of the kinetic energy + the potential energy

$$E = \text{K.E.} + V \Rightarrow \text{K.E.} = E - V$$

But the kinetic energy = $(1/2)mv^2$, so

$$\frac{1}{2}mv^2 = E - V \Rightarrow v^2 = \frac{2}{m}(E - V)$$

Substituting for v^2 in Eq. (5.14) gives the well-known form of the Schrödinger equation,

$$\nabla^2\psi + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0$$

Note that comparison with short form of Schrödinger equation

$$\hat{H}\psi = E\psi$$

shows that Hamiltonian operator can be given by

$$\hat{H} = \frac{h^2}{8\pi^2 m}\nabla^2 + V$$

Hydrogen Atom and the Schrödinger Equation

The solution to the Schrödinger's wave equation for hydrogen atom gives the possible energy level that the electron may occupy and the corresponding wave function ψ.

$$\nabla^2\psi + \frac{8\pi^2 m}{h^2}(E - V)\,\psi = 0$$

Acceptable solutions to the wave equation, that is, solutions which are physically possible, must have certain properties:

1. ψ must be continuous.
2. ψ must be finite.
3. ψ must be single valued.
4. The probability of finding an electron at a point x, y, z over all space $\int_{-\infty}^{+\infty} \psi^2\, \mathrm{d}x\, \mathrm{d}y\, \mathrm{d}z = 1$.

Several wave functions called ψ_1, ψ_2, ψ_3, …, will satisfy these conditions to the wave equation, and each of these has a corresponding energy levels E_1, E_2, E_3, …, which an electron can occupy which are quantized. Each of these wave functions ψ_1, ψ_2, …, is called an *orbital*, by analogy with the *orbits* in the Bohr theory. In a hydrogen atom, the single electron normally occupies the lowest of the energy levels E_1. This is called the ground state. The corresponding wave function ψ_1 describes the orbital, that is, the region in space where there is a high probability of finding the electron. For a one-electron system such as hydrogen, the **probability** of finding an electron at a point within the atom is $|\psi|^2$.

Note: The amplitude is squared because, mathematically, the amplitude can be either positive or negative, but probability only makes sense if it is positive. Squaring the amplitude assures us that the probabilities will be positive.

The quantum mechanical theory can predict and explain all the observations regarding hydrogen spectrum including those not explained by Bohr's theory. The application of Schrödinger's wave equation to multi-electron systems is somewhat more complicated and its solution is not easily obtained.

Important Features of Quantum Mechanical Model

Important features of quantum mechanical model are:

1. The energy of electrons in an atom is quantized, that is, they can have only specific values when bound to nucleus in an atom. The quantized energy levels of the electrons result from the wave nature of electrons (de Broglie's dual behavior of matter).
2. All the information about a particle (electron) in a given energy level is contained in the wave function ψ which corresponds to the allowed (physically possible) solutions of the Schrödinger wave equation.
3. Since it is not possible to determine both the exact position and velocity of the electron in an atom (Heisenberg's uncertainty principle), the path of an electron in atom cannot be determined accurately. Hence, the concept of probability of finding the electron at a point is introduced in quantum mechanics.
4. The probability of finding an electron in an atom is proportional to $|\psi|^2$, that is, the square of wave function and is known as probability density. It always has a positive value and the value at different points in atom corresponds to region around the nucleus where the electron is most likely to be found.
5. The wave function and its square $|\psi|^2$ have values for all locations about the nucleus. For hydrogen atom, $|\psi|^2$ is large near the nucleus and decreases with increase in distance away from the nucleus. This indicates that the probability of finding the electron is the maximum near the nucleus and decreases as the distance from nucleus increases. The value becomes extremely small with increasing distance but at no point, it becomes zero.
6. The wave function ψ obtained by solving Schrödinger equation for an electron in an atom corresponds to the atomic orbital. Since the equation can have many solutions, there are various possible wave functions ψ for an electron and hence many possible atomic orbitals. These orbitals form the basis of electronic structure of atoms. Each orbital has a definite energy and can accommodate two electrons.
7. In multi-electron atoms, the electrons are filled in various orbitals in increasing order of energy.
8. For a given type of atom, there are a number of solutions to the wave equation which are acceptable, and each orbital may be described uniquely by a set of three quantum numbers, n (principal quantum number), l (azimuthal quantum number) and m_l (magnetic quantum number).
9. A node is defined as point where the probability of finding an electron is zero. If it is a plane where probability of finding an electron is zero, then it is known as nodal plane. If it is a surface at which probability of finding the electron is zero, then it is known as the nodal surface. The value of ψ^2 will be zero at any node.

Solved Example 5-45

The Schrödinger wave equation for hydrogen atom is

$$\psi_{2s} = \frac{1}{4(2\pi)^{1/2}}\left(\frac{1}{a_0}\right)^{3/2}\left(2-\frac{r}{a_0}\right)e^{-r/a}$$

where a_0 is Bohr's radius. Let the radial node in 2*s* be at r_0. Then find r in terms of a_0. **(IIT–JEE 2004)**

Solution

The probability of finding 2*s* electron will be

$$\psi_{2s}^2 = \frac{1}{32\pi}\left(\frac{1}{a_0}\right)^3\left(2-\frac{r}{a_0}\right)^2 e^{-2r/a_0}$$

Node is a point where probability of finding an electron is zero. Thus, $\psi_{2s}^2 = 0$ when $r = r_0$. Therefore,

$$\frac{1}{32\pi}\left(\frac{1}{a_0}\right)^2\left(2-\frac{r_0}{a_0}\right)^2 e^{-2r/a_0} = 0$$

The only factor that can be zero is

$$2-\frac{r_0}{a_0} = 0 \quad \Rightarrow r_0 = 2a_0$$

Solved Example 5-46

(a) Write down the general form of the Schrödinger equation and define each of the terms in it.

(b) Solutions to the wave equation that are physically possible must have four special properties. What are they?

Solution

(a) The general form of the Schrödinger wave equation is

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2 m}{h^2}(E-V)\psi = 0$$

where ψ is the amplitude of the wave, E is the total energy of the electron, V is the potential energy, m is the mass of the electron, h is the Planck's constant and $\partial^2\psi/\partial x^2$ (or $\partial^2\psi/\partial y^2$ or $\partial^2\psi/\partial z^2$) is the second differential of ψ.

(b) They are four quantum numbers, that is, principal quantum number, azimuthal quantum number, magnetic quantum number and spin quantum number. The conditions for the solution of a wave function to be valid are: that the wave function must be continuous, finite and single valued.

5.16 | RADIAL AND ANGULAR WAVE FUNCTIONS

The Schrödinger equation can be solved completely for the hydrogen atom, and for related ions which have only one electron such as He$^+$ and Li^{2+}. For other atoms only approximate solutions can be obtained. For most calculations, it is simpler to solve the wave equation if the Cartesian coordinates x, y and z are converted into polar coordinates r, θ and ϕ. The coordinates of the point A measured from the origin are x, y, and z in Cartesian coordinates, and r, θ and ϕ in polar coordinates. It can be seen from Fig. 5.25 that the two sets of coordinates are related by the following expressions:

$$z = r\cos\theta \quad y = r\sin\theta\sin\phi \quad x = r\sin\theta\cos\phi$$

The Schrödinger equation is usually written:

$$\nabla^2\psi + \frac{8\pi^2 m}{h^2}(E-V)\psi = 0$$

where $$\nabla^2\psi = \frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}$$

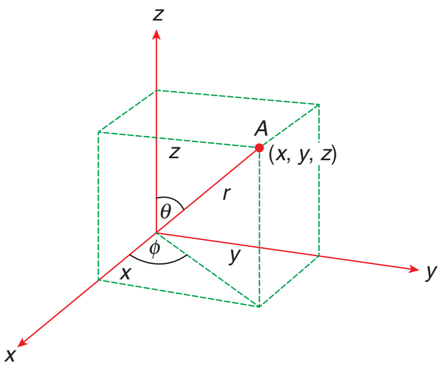


Figure 5.25 The relationship between cartesian and polar coordinates.

Changing to polar coordinates, $\nabla^2\psi$ becomes

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{r^2\sin^2\theta}\cdot\frac{\partial^2\psi}{\partial\phi^2}+\frac{1}{r^2\sin\theta}\cdot\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)$$

The solution of this is of the form

$$\psi = R(r)\cdot\Theta(\theta)\cdot\Phi(\phi) \tag{5.17}$$

where $R(r)$ is a function that depends on the distance from the nucleus, which in turn depends on the quantum numbers n and l. ↑(θ) is a function of θ, which depends on the quantum numbers l and m. $\Phi(\phi)$ is a function of ϕ, which depends only on the quantum number m. Equation (5.18) may be rewritten as

$$\psi = R(r)_{nl}\cdot A_{ml} \tag{5.18}$$

This splits the wave function into two parts which can be solved separately:

1. $R(r)$ the radial function, which depends on the quantum numbers n and l.
2. A_{ml} the total angular wave function, which depends on the quantum numbers m and l.

Radial Distribution Curve

1. Since we are only plotting the radial part of the curve, therefore

$\psi = R(r)$ Radial wave function

$\psi^2 = R^2(r)$ Radial probability density

$\psi^2\cdot 4\pi r^2 dr = R^2(r)4\pi r^2 dr$ Radial probability distribution

$$\psi^2 = \frac{\text{Probability}}{\mathrm{d}V}$$

In Fig. 5.26, the small segment of volume $\mathrm{d}V$ is given by

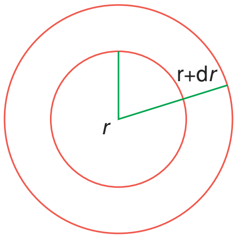


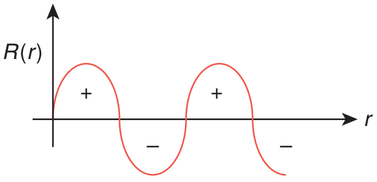
Figure 5.26

$$\begin{aligned}\mathrm{d}V &= \frac{4}{3}\pi(r+\mathrm{d}r)^3 - \frac{4}{3}\pi r^3\\ &= \frac{4}{3}\pi r^3 + \frac{4}{3}\pi r^2\times 3\,\mathrm{d}r + \frac{4}{3}\pi(3r)(\mathrm{d}r)^2 + \frac{4}{3}\pi(\mathrm{d}r)^3 - \frac{4}{3}\pi r^3\\ &\approx 4\pi r^2\,\mathrm{d}r\end{aligned}$$

Since $\psi^2\cdot\mathrm{d}V = \text{Probability} = \psi^2 4\pi r^2\mathrm{d}r$

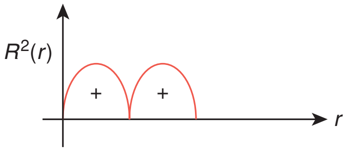
2. Total number of radial nodes = $n-l-1$
Total number of angular nodes = l
Therefore, total number of nodes = $n-1$
In the radial distribution curve we only take radial nodes, that is, $n-l-1$
This is under the assumption that $r = 0$ (nucleus) and $r = \infty$ are not nodes. (If both both of them to be considered, then radial nodes = $n-l-1+2 = n-l+1$).

3. The value of ψ or $R(r)$ varies as +, –, +, –, as shown in Fig. 5.27(a).



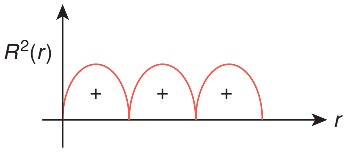
(a)

The value of ψ^2 or $R^2(r)$ is always positive as shown in Fig. 5.27(b).



(b)

The value of $\psi^2 \cdot 4\pi r^2 \mathrm{d}r$ or $R^2(r)4\pi r^2\, \mathrm{d}r$ is always positive as shown in Fig. 5.27(c).



(c)

Figure 5.27 The value of (a) ψ or $R(r)$; (b) ψ^2 or $R^2(r)$ and (c) $\psi^2 \cdot 4\pi r^2$ or $R^2(r)\, 4\pi r^2\, \mathrm{d}r$ as a function of r.

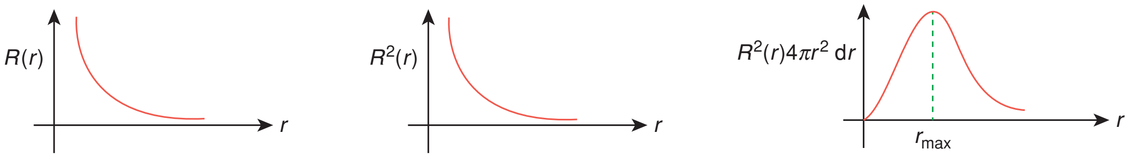
4. The value of $R(r)$ and $R^2(r)$ decreases with increase in r. The value of $R^2(r)4\pi r^2 \mathrm{d}r$ increases with increase in r.

5. For s orbital, values of $R(r)$ and $R^2(r)$ are non-zero at $r = 0$.
   For p, d and f orbitals, values of $R(r)$ and $R^2(r)$ are zero at $r = 0$.

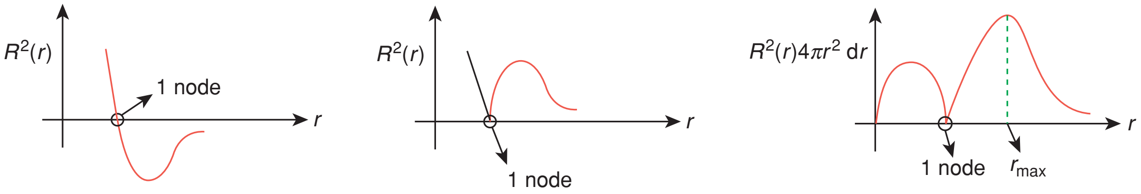
6. $r_{\max}$ is the distance from the nucleus at which total probability of finding an electron is the maximum.

Consider the radial parts of the distribution curve for radial wave function, radial probability density and radial probability distribution for the following orbitals in Fig. 5.28.

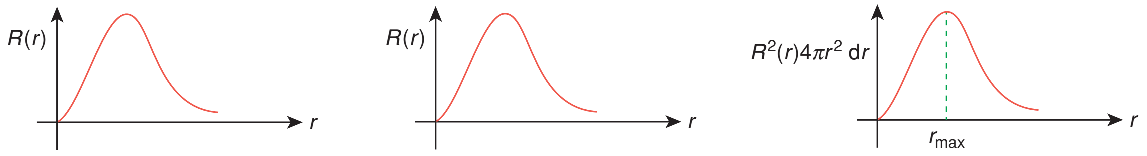
1. For 1s: $n = 1, l = 0, n - l - 1 = 0$



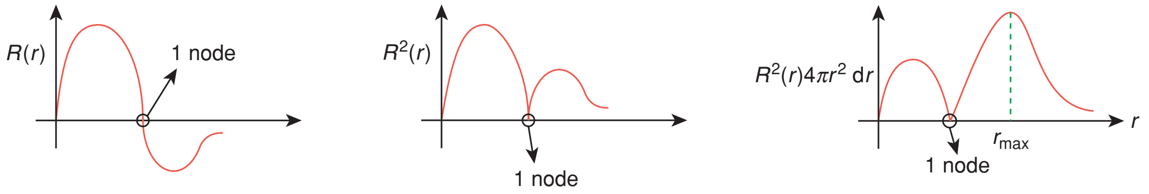
2. For 2s: $n = 2, l = 0, n - l - 1 = 2 - 0 - 1 = 1$



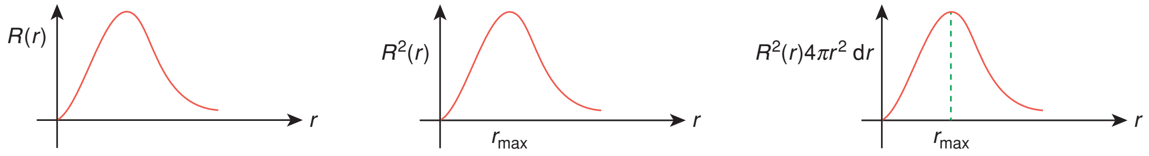
3. For $2p$: $n = 2, l = 1, n - l - 1 = 0$



4. For $3p$: $n = 3, l = 1, n - l - 1 = 1$



5. For $3d$: $n = 3, l = 2, n - l - 1 = 0$



6. For $4d$: $n = 4, l = 2, n - l - 1 = 1$

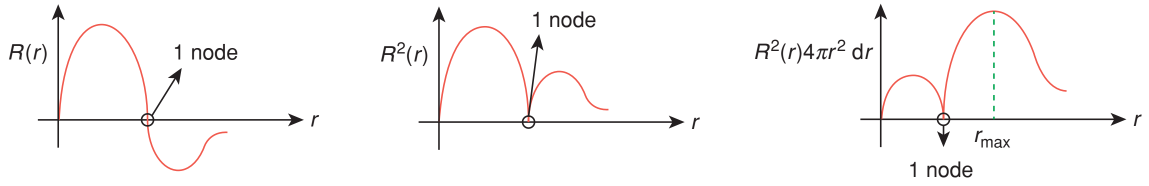


Figure 5.28 Radial part of distribution curve for different orbitals.

Consider the following radial probalility distribution curve made of $4d$ and $3p$ orbitals as shown in Fig. 5.29. Then the curve corresponding to each orbital can be identified as follows.

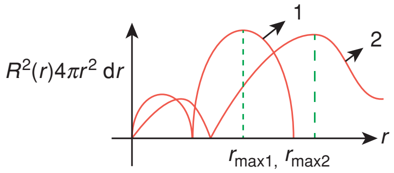


Figure 5.29 Radial probability distribution curve for $3p$ and $4d$ orbitals.

As n increases $r_{\max}$ increases, therefore, $r_{\max}$ of $4d > r_{\max}$ of $3p$. Thus, curve 2 represents $4d$ and curve 1 represents $3p$ orbitals, respectively.

Note: If n is the same for any orbital, then $r_{\max}$ of $s > p > d > f$. For example, $r_{\max}$ for $4s > 4p > 4d$.

Plot of Angular Wave Function

The angular wave function A depends only on the direction, and is independent of the distance from the nucleus (r). Thus, A^2 is the probability of finding an electron at a given direction θ, ϕ at any distance from the nucleus to infinity. The angular functions A are plotted as polar diagrams in Fig. 5.30 It must be emphasized that *these polar diagrams* ***do not*** *represent the total wave function* ψ, but only the angular part of the wave function.

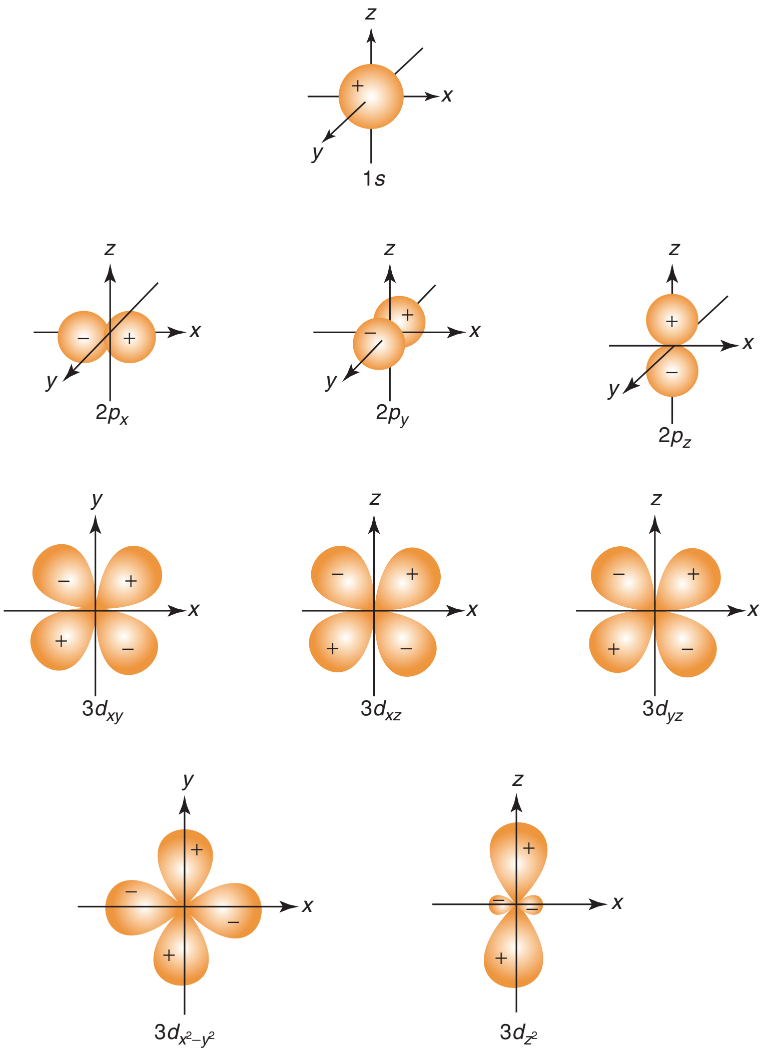


Figure 5.30 Boundary surface for the angular part of the wave function $A(\theta, \phi)$ for the 1*s*, 2*p* and 3*d* orbitals for a hydrogen atom shown as polar diagrams.

Note: Polar diagrams are commonly used to illustrate the overlap of orbitals giving bonding between atoms. These diagrams are suitable for this purpose, as they show the signs + and – relating to the symmetry of the angular function. For bonding, like signs must overlap.

Some important features of angular wave function plots are:

1. It is difficult to picture an angular wave function as a mathematical equation. It is much easier to visualize a boundary surface, that is, a solid shape, which for example contains 90% of the electron density. To emphasize that ψ is a continuous function, the boundary surfaces have been extended up to the nucleus in Fig. 5.30. For *p* orbitals the electron density is zero at the nucleus, and some texts show a *p* orbital as two spheres which do not touch.

2. These diagrams show the symmetry for the 1*s*, 2*p*, 3*d* orbitals. However, in the others, 2*s*, 3*s*, 4*s* … , 3*p*, 4*p*, 5*p* … , 4*d*, 5*d* …. the sign (symmetry) changes inside the boundary surface of the orbital. This is readily seen as nodes in the graphs of the radial functions (Fig. 5.29).
3. The probability of finding an electron at a direction θ, ϕ is the wave function squared, A^2, or more precisely $\psi_\theta^2\,\psi_\phi^2$. The diagrams in Fig. 5.30 are of the angular part of the wave function A, not A^2. Squaring does not change the shape of an *s* orbital, but it elongates the lobes of *p* orbitals (Fig. 5.31).

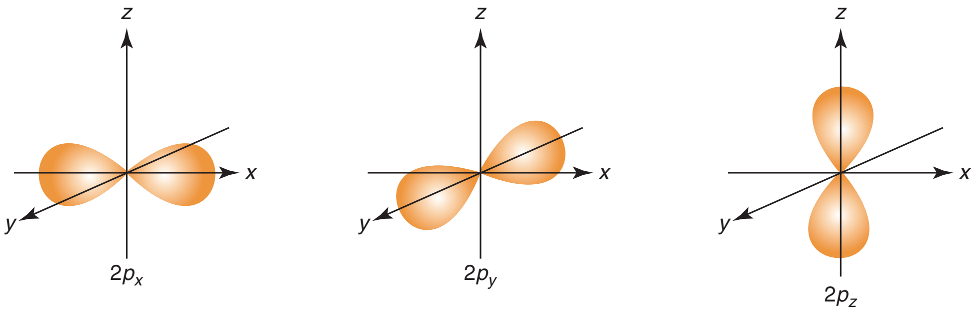


Figure 5.31 The angular part of the wave function squared $A^2(\theta, \phi)$ for the 2*p* orbitals for a hydrogen atom.

Plot of Total Wave Function

The total wave function is made up from contributions from both the radial and the angular functions.

$$y = R(r)\cdot A$$

Thus, the probability of finding an electron simultaneously at a distance *r* and in a given direction θ, ϕ is given by

$$\psi^2_{r,\theta,\phi} = R^2(r)\cdot A^2(\theta, \phi)$$

A full representation of the probability of finding an electron requires the total wave function squared and includes both the radial and angular probabilities squared. It really needs a three-dimensional model to display this probability, and show the shapes of the orbitals. It is difficult to do this adequately on a two-dimensional piece of paper, but a representation is shown in Fig. 5.32.

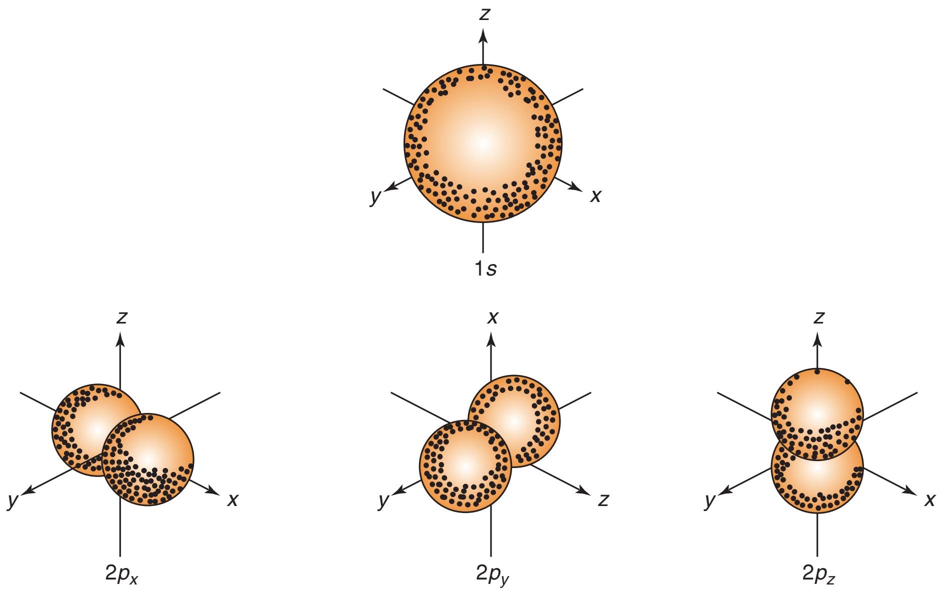


Figure 5.32 Total wave function (orbitals) for hydrogen.

The **azimuthal** or **subsidiary quantum number** (also known as **orbital angular momentum**) is represented by l and describes the three-dimensional shape of the orbital occupied by the electron. The quantum number l may have values 0, 1, 2, … $(n - 1)$. When $l = 0$, the orbital is spherical and is called an *s* orbital; when $l = 1$, the orbital is dumbbell-shaped and is called a *p* orbital; when $l = 2$, the orbital is double dumbbell-shaped and is called a *d* orbital and when $l = 3$ a more complicated *f* orbital is formed. Each shell has one or more subshells which depend on the value of n. For $n = 1$, there is only one subshell, which corresponds to $l = 0$. For $n = 2$, here are two subshells corresponding to $l = 0, 1$. For $n = 3$, the number of subshells is three corresponding to $l = 0, 1, 2$. The subshells corresponding to various values of l are listed as follows

Value for l	0	1	2	3	4	5
Notation for subshell	*s*	*p*	*d*	*f*	*g*	*h*

The **magnetic quantum number** (m_l) is used to describe the orientation in space of a degenerate orbital. (It is called the *magnetic* quantum number because the effect of different orientations of orbitals was first observed in the presence of a magnetic field.). It is given by $2l + 1$ (Table 5.5).

Table 5.5 Atomic orbitals

Principal quantum number n	Subsidiary quantum number l	Magnetic quantum numbers m_e	Symbol
1	0	0	1*s* (one orbital)
2	0	0	2*s* (one orbital)
2	1	−1, 0, +1	2*p* (three orbitals)
3	0	0	3*s* (one orbital)
3	1	−1, 0, +1	3*p* (three orbitals)
3	2	−2, −1, 0, +1, +2	3*d* (five orbitals)
4	0	0	4*s* (one orbital)
4	1	−1, 0, +1	4*p* (three orbitals)
4	2	−2, −1, 0, +1, +2	4*d* (five orbitals)
4	3	−3, −2, −1, 0, +1, +2, −3	4*f* (seven orbitals)

Selection Rules Governing Allowed Combinations of Quantum Numbers

Atomic spectra have shown that electrons in atoms occupy discrete energy states or energy levels. The quantum mechanical model allows only certain combinations of quantum numbers to describe these states. The allowed combinations of quantum numbers can be determined from the following set of rules.

1. The three quantum numbers (n, l and m_l) are all integers.
2. The principal quantum number (n) cannot be zero. The allowed values of n are therefore 1, 2, 3, 4, ….
3. The angular quantum number (l) can be any integer between 0 and $n - 1$. If $n = 3$, for example, l can be either 0, 1 or 2.
4. The magnetic quantum number (m_l) can be any integer between $-l$ and $+l$. If $l = 2$, m_l can be −2, −1, 0, 1 or 2.

The information provided by the four quantum numbers is summed up in Table 5.6.

Table 5.6 Information obtained from the four quantum numbers

Principal quantum number (n)	Azimuthal quantum number (l)	Magnetic quantum number (m_l)
The main shell in which the electron resides	The number of subshells present in the *n*th shell	The number of orbitals present in each subshell or the orientation of the subshells
The energy of the orbital	The energy of the orbital in a multi-electron system	
Approximate distance of the electron from the nucleus	Shape of the orbitals	

(*Continued*)

Table 5.6 (Continued)

Principal quantum number (n)	Azimuthal quantum number (l)	Magnetic quantum number (m_l)
The maximum number of electrons present in the shell	For a given value of n, l can have values from 0 to $n - 1$. In each subshell, there are $(2l + 1)$ types of orbitals	For a given value of l, $m = -l$ to $+l$
Represented by integers 1, 2, 3, … or K, L, M, N, etc.	$l = 0$, s subshell $l = 1$, p subshell $l = 2$, d subshell $l = 3$, f subshell	For s subshell: s For p subshell: p_x, p_y, p_z For d subshell: $d_{xy}, d_{yz}, d_{xz}, d_{z^2}, d_{x^2-y^2}$
Accounts for the main lines in the atomic spectrum	Accounts for the fine lines in the atomic spectra	Accounts for the splitting of lines in the atomic spectrum

Shapes of Atomic Orbitals

An electron behaves as if it were spread out around the nucleus in a sort of **electron cloud**. Three things are important to understand how electron density distributes itself in atomic orbitals, the *shape* of the orbital, its *size,* and its *orientation* in space relative to other orbitals. The electron density in an orbital does not end abruptly at some particular distance from the nucleus. It gradually fades away. Therefore, to define the size and shape of an orbital, it is useful to picture some imaginary surface enclosing, say, 90% of the electron density of the orbital, and on which the probability of finding the electron is everywhere the same.

For the 1s orbital, we find that if we go out a given distance from the nucleus in *any* direction, the probability of finding the electron is the same. Figure 5.33 is a **dot-density diagram** that illustrates the way the probability of finding the electron varies in space for a 1s orbital. In those places where the dot density is large (i.e., where there are large numbers of dots per unit volume), the amplitude of the wave is large and the probability of finding the electron is also large. This means that all the points of equal probability lie on the surface of a sphere, so we can say that the shape of the orbital is spherical.

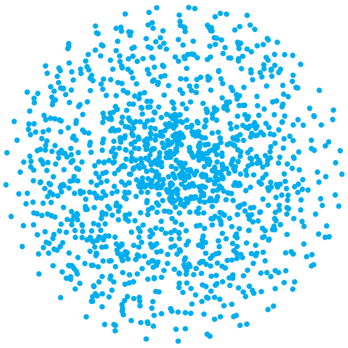


Figure 5.33 A dot-density diagram that illustrates the electron probability distribution for a 1s electron.

In fact, all s orbitals are spherical but their sizes increase with increasing n. This is illustrated in Fig. 5.34. Notice that beginning with the 2s orbital, there are certain places where the electron density drops to zero. These are spherical-shaped nodes of the s orbital electron waves which consist of imaginary spherical *surfaces* on which the electron density is zero. The orbitals become larger as the principal quantum number, n, becomes larger. All the s orbitals except the first one (1s) have a shell-like structure, rather like an onion or a hailstone, consisting of concentric layers of electron density.

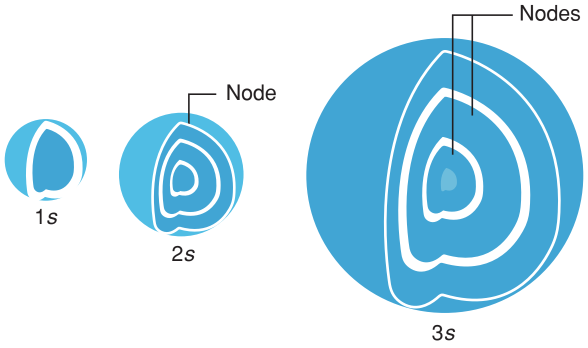


Figure 5.34 Size variations among s orbitals.

For the p orbitals the electron density is equally distributed in two regions on opposite sides of the nucleus. Figure 5.35(a) illustrates the dot-density diagram showing two "lobes" of *one* 2p orbital. Between the lobes is a **nodal plane** – an imaginary flat surface on which every point has an electron density of zero. The size of the p orbitals also increases with increasing n as illustrated by the cross-section of a $3p$ orbital in Fig. 5.35(b). The $3p$ and higher p orbitals have additional nodes besides the nodal plane that passes through the nucleus.

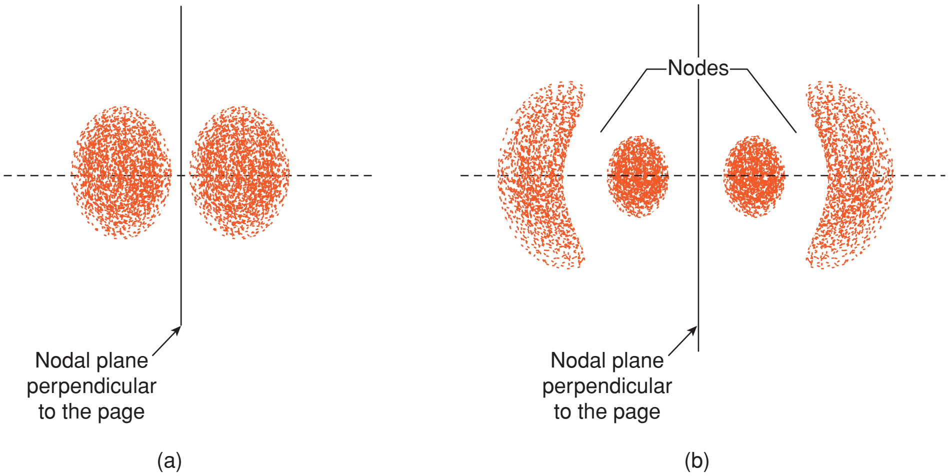

Nodes
Nodal plane perpendicular to the page
Nodal plane perpendicular to the page
(a)
(b)

Figure 5.35 Distribution of electron density in p orbitals.

Similarly, Fig. 5.36(a) illustrates the shape of a surface of constant probability for a $2p$ orbital and Fig. 5.36(b) is a simplified representation of a p orbital that emphasizes the directional nature of the orbital.

A p subshell consists of three orbitals of equal energy. Wave mechanics tells us that the lines along which the orbitals have their maximum electron densities are oriented at 90° to each other, corresponding to the axes of an imaginary xyz coordinate system (Fig. 5.37). For convenience, in referring to the individual p orbitals they are often labeled according to the axis along which they lie. The p orbital concentrated along the x axis is labeled p_x, and so forth.

The shapes of the d orbitals, illustrated in Fig. 5.38, are a bit more complex than are those of the p orbitals. Because of this, and because there are five orbitals in a d subshell, we have not attempted to draw all of them at the same time on the same set of coordinate axes. Notice that four of the five d orbitals have the same shape and consist of four lobes of electron density. These four d orbitals each have two perpendicular nodal planes that intersect the nucleus. These orbitals differ only in their orientations around the nucleus (their labels come from the mathematics of wave mechanics). The fifth d orbital, labeled d_{z^2}, has two lobes that point in opposite directions along the z axis plus a doughnut-shaped ring of electron density around the center that lies in the xy plane. The two nodes for the d_{z^2} orbital are conic surfaces whose peaks meet at the nucleus.

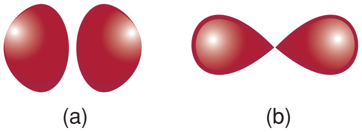


Figure 5.36 Representations of the shapes of p orbitals.

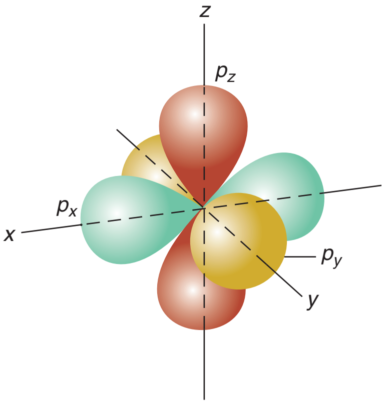


Figure 5.37 The shape of the three p orbitals in a p subshell.

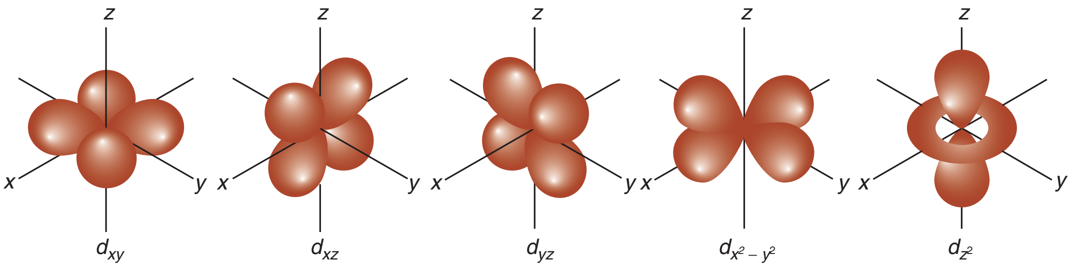


Figure 5.38 The shapes and directional properties of the five d orbitals of a d subshell.

Names of Nodal Planes in p and d Orbitals and Nodal Surfaces

Nodal plane in $p_x = yz$ nodal plane (Nodal plane along the axis)
Nodal plane in $p_y = xz$ nodal plane (Nodal plane along the axis)
Nodal plane in $p_z = xy$ nodal plane (Nodal plane along the axis)
Nodal plane in $d_{xy} = xz$ and yz nodal plane (Nodal plane at 45° to the axis)
Nodal plane in $d_{yz} = xy$ and xz nodal plane (Nodal plane at 45° to the axis)
Nodal plane in $d_{xz} = xy$ and yz nodal plane (Nodal plane at 45° to the axis)
Nodal plane in $d_{x^2-y^2} = xy$ and yz nodal plane (Nodal plane along the axis)

Electron Spin and Spin Quantum Number

The presence of the fourth quantum number was proposed in 1925 by George Uhlenbeck and Samuel Goudsmit in 1925. In an experiment conducted by Stern and Gerlach, when a beam of atoms with an odd number of electrons is passed through an uneven magnetic field, the beam is split in two. The splitting occurs because the electrons within the atoms interact with the magnetic field in two different ways. Based on experimental observations, they postulated that the electron had an intrinsic angular momentum, independent of its orbital characteristics. The electrons behave like tiny magnets, and they are attracted to one or the other of the poles depending on their orientation. This can be explained by imagining that an electron spins around its axis, like a toy top. A moving charge creates a moving electric field, which in turn creates a magnetic field. The spinning electrical charge of the electron creates its own magnetic field. This **electron spin** could occur in two possible directions, which accounted for the two beams.

Electrons do not actually spin but the magnetic properties of electrons are just what we would see if the electron were a spinning charged particle, and it is useful to picture the electron as spinning. The concept of electron spin led to the fourth quantum number for the electron, called the **spin quantum number, m_s**, which can take on two possible values: $m_s = +1/2$ or $m_s = -1/2$, corresponding to the two beams.

The **spin quantum number** m_s refers to the two possible orientations of the spin axis of an electron and can take the values +1/2 and −1/2 for a given value of m. An electron spins around its own axis (like the earth) while moving around the nucleus in its orbital. This electronic spin gives rise to a circulating electric charge that generates a magnetic field. The spin angular momentum of the electron is a vector that can take two values (+1/2 and −1/2) corresponding to the two spin states of the electron. +1/2 or −1/2 may not necessarily imply spin up or spin down. It is ok even to assign +1/2 to spin down and vice versa. An orbital can contain a maximum of two electrons and there are two possible spin states, so the electrons present in one orbital will always have opposite spins. It accounts for magnetic properties of substances.

Solved Example 5-48

Find the velocity (m s^{-1}) of electron in first Bohr's orbit of radius a_0. Also find the de Broglie's wavelength (in m). Find the orbital angular momentum of $2p$ orbital of hydrogen atom in units of $h/2\pi$. **(IIT-JEE 2005)**

Solution

Since $mvr = nh/2\pi$ and $r = a_0 = 0.529$ Å, we have the velocity of the electron as

$$v = \frac{nh}{2\pi mr} = \frac{6.626\times10^{-34}}{2\times3.14\times9.1\times10^{-31}\times0.529\times10^{-10}}$$
$$= 2.18\times10^{6}\ \text{m s}^{-1}$$

as for hydrogen atom, $Z = 1$, $n = 1$. Now, the de Broglie's wavelength is

$$\lambda = \frac{h}{mv} = \frac{6.26\times10^{-34}}{9.1\times10^{-31}\times2.18\times10^{6}} = 3.34\times10^{-10}\ \text{m} = 3.3\ \text{Å}$$

For $2p$, $l = 1$, so the orbital angular momentum is

$$\sqrt{l(l+1)}\,\frac{h}{2\pi} = \sqrt{2}\,\frac{h}{2\pi}$$

Solved Example 5-49

Write down the values of quantum numbers of all the electrons present in the outermost orbit of neon (atomic number 10).

Solution

The electronic configuration of neon is $1s^2, 2s^2, 2p^6$. Values of quantum numbers are as follows. The outermost orbit has $n = 2$ and $l = 0$ to $n - 1$.

	n	l	m	s
$2s^2$	2	0	0	+ 1/2, –1/2
$2p_x^2$	2	1	±1	+ 1/2, –1/2
$2p_y^2$	2	1	±1	+ 1/2, –1/2
$2p_z^2$	2	1	0	+ 1/2, –1/2

Solved Example 5-50

(a) An electron is in 6*f* orbital. What possible values of quantum numbers n, l, m and s can it have?

(b) What designation is given to an orbital having (i) $n = 2, l = 1$ and (ii) $n = 3, l = 0$?

Solution

(a) For an electron in 6*f* orbital, quantum numbers are:

$n = 6$	$l = 0$	$m = 0$
	$l = 1$	$m = -1, 0, +1$
	$l = 2$	$m = -2, -1, 0, +1, +2$
	$l = 3$	$m = -3, -2, -1, 0, +1, +2, +3$
	$l = 4$	$m = -4$ to $+4$ including 0
	$l = 5$	$m = -5$ to $+5$ including 0

(b) The designations are (i) 2*p* and (ii) 3*s*.

Solved Example 5-51

Using *s*, *p*, *d*, *f* notations, describe the orbital with the following quantum numbers: **(a)** $n = 2$, $l = 1$; **(b)** $n = 4$, $l = 0$; **(c)** $n = 5, l = 3$; **(d)** $n = 3, l = 2$.

Solution

The orbitals are

	n	l	Orbitals
(a)	2	1	2*p*
(b)	4	0	4*s*
(c)	5	3	5*f*
(d)	3	2	3*d*

Solved Example 5-52

What is the maximum number of electrons that may be present in all the atomic orbitals with principle quantum number 3 and azimuthal quantum number 2?

(IIT-JEE 1985)

Solution

For $n = 3$ and $l = 2$ (i.e., 3*d* orbital), the values of m varies from –2 to +2, that is, –2, –1, 0, +1, +2 and for each m there are 2 values of s, that is, +1/2 and –1/2. The maximum number of electrons in all the five *d*-orbitals is 10.

Energies of Orbitals

In case of hydrogen, the energy of electron is determined only by the principal quantum number. The energy of all the orbitals in a given shell is the same, irrespective of the shape of the orbital. Thus, the order of energy levels is

$$1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f$$

The orbitals having the same energy are known as degenerate orbitals. The electron in hydrogen atom in its most stable state resides in the 1*s* orbital and this state is referred to as the ground state and the electron is most strongly held by the nucleus in this state. When the electron is raised to higher energy states, such as 2*s*, 2*p*, etc., it is said to be in the excited state.

In case of multi-electron atoms, the energy of an electron is determined by both the principal quantum number and the azimuthal quantum number, that is, it depends on both the shell as well as the subshell. For a given principal quantum number, *s*, *p*, *d* and *f* orbitals will have different energies. The relative energies of electron in an atom containing two or more electrons is shown in Fig. 5.39.

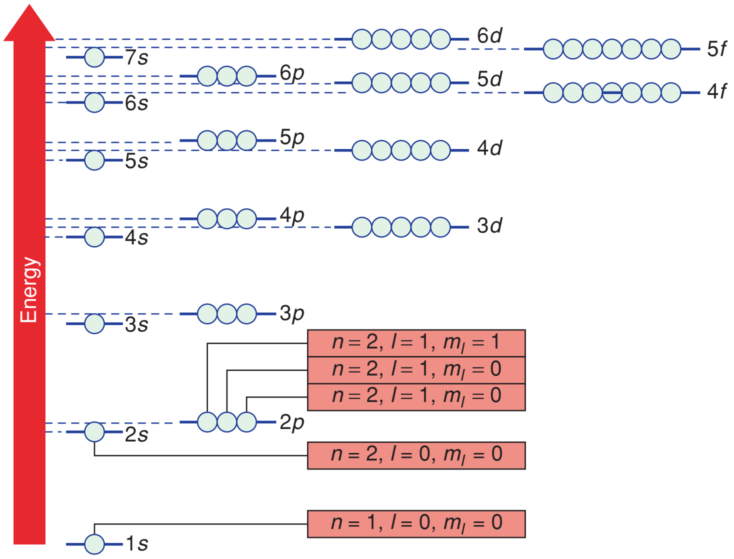


Figure 5.39 Energy level diagram for atoms with two or more electrons.

The important observations from the energy level diagram are:

1. All the orbitals of a given subshell have the *same* energy.
2. In going upwards on the energy scale, the spacing between successive shells decreases as the number of subshells increases. This leads to some overlapping of shells having different values of *n*. For instance, the 4*s* subshell is lower in energy than the 3*d* subshell, 5*s* is lower than 4*d*, and 6*s* is lower than 5*d*. In addition, the 4*f* subshell is below the 5*d* subshell and 5*f* is below 6*d*.

Solved Example 5-53

Within any given shell, how do the energies of the *s*, *p*, *d* and *f* subshells compare? What fact about the energies of subshells was responsible for the apparent success of Bohr's theory about electronic structure?

Solution

The energies of *s*, *p*, *d* and *f* subshells increase in the order as $s < p < d < f$. The success of the Bohr's theory lies in the fact that the energies of the orbitals were arranged according to their shell value, that is, *s* being more close to the nucleus has the least energy while *f* being farthest has the maximum energy.

Solved Example 5-54

What are the two properties of orbitals in which we are most interested? Why?

Solution

The two properties of orbitals in which we are most interested are their shapes and energies. Their energies are important because we normally find atoms in their most stable states, which we call their ground states, in which electrons are at their lowest possible energies.

Effective Nuclear Charge

In case of hydrogen or hydrogen-like species, only attractive electronic forces between negatively charged electrons and positively charged nucleus are present. In case of multi-electron atoms, in addition to these forces of attraction, forces of repulsion exist between negatively charged electrons and positively charged nucleus. The atom is stable because the total attractive forces of interaction are more than the repulsive forces. The attractive forces of interaction increase with increase in positive charge (Ze) on the nucleus. However, the electrons in the outer shell are not able to experience the full force of attraction of the positive charge on nucleus due to presence of intervening inner orbital electrons. This is known as the **shielding** of the outer electrons of an atom from the positive charge of nucleus by the inner shell electrons. The net positive charge experienced by the outer shell electrons due to shielding effect is known as the **effective nuclear charge** (Z_{eff}). Despite the shielding effect, the attractive forces experienced by the outer electrons increase with increase in atomic number (Z).

The effective nuclear charge experienced by the outer electrons depends on the shell and shape of orbitals in which the electrons are present. Some important features are as follows:

1. Within the same shell, electrons in the *s* orbitals shield the outer shell electrons from positive charge of the nucleus more effectively than the *p* orbitals due to their symmetrical shape. Similarly, the shielding effect of electrons in *p* orbitals is more than that of the *d* orbitals due to their shape.
2. The electron in *s* orbital spends more time closer to the nucleus as compared to electron in a *p* orbital due to its spherical shape and electrons in *p* orbital spend more time near the nucleus than electrons in *d* orbitals. Thus for a given principal quantum number, the effective positive nuclear charge decreases with increase in azimuthal quantum number.
3. The $(n + l)$ rule is used for determining the energies of different orbitals. Lower the $(n + l)$ value for an orbital, lower is the energy.
4. Similar orbital in different atoms have different energies because the effective nuclear charge is different. The energies of similar orbitals decrease with increase in nuclear charge.

Rules to Calculate Effective Nuclear Charge

1. Write down the electronic configuration of the element.
2. Fill the electrons according to Aufbau's principle.
3. For shielding constant, the electrons to the right of the electron under consideration are not taken into account.
4. The shielding constant is calculated as follows:
   (a) All other electrons present in the same group as the electron under consideration provide shielding of 0.35 nuclear charge units. Group 1*s* is the exception here. The other electron contributes only 0.30 nuclear charge units.
   (b) If the group is of the *s*, *p* type, an amount of 0.85 units from each electron of $(n - 1)$ shell and an amount of 1.00 unit for each electron of $(n - 2)$ and lower shell.
   (c) If the group is of the *d* or *f* type then an amount of 1.00 unit for each electron from all electrons lying left to that orbital.

Solved Example 5-55

Calculate the effective nuclear charge in nitrogen for 2*p* electron.

Solution

Electronic configuration of nitrogen is $1s^2 2s^2 2p^3$.
Screening constant, $\sigma = (0.35 \times 4) + (0.85 \times 2) = 3.10$
Effective nuclear charge, $Z_{\text{eff}} = Z - \sigma = 7 - 3.10 = 3.90$

Solved Example 5-56

Calculate the effective nuclear charge in zinc for 4*s* electron and for 3*d* electron.

Solution

Electronic configuration of zinc is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$.

For 4*s* electron, $\sigma = (0.35 \times 1) + (0.85 \times 18) + (1 \times 10) = 25.65$

$$Z_{\text{eff}} = Z - \sigma = 30 - 25.65 = 4.35$$

For 3*d* electron, $\sigma = (0.35 \times 9) + (1 \times 18) = 21.15$

$$Z_{\text{eff}} = Z - \sigma = 30 - 21.15 = 8.85$$

5.18 | ELECTRONIC CONFIGURATION OF ATOMS

Aufbau Principle

In the case of atoms, electrons occupy the available orbitals in the subshells of lowest energy. This is known as the Aufbau principle (from the German for "building up"). The assignment of all the electrons in an atom into specific shells and subshells is known as the element's electron configuration (Fig. 5.40).

It is important to know the sequence in which the energy levels are filled. Figure 5.39 is a useful aid, which shows the order of filling of energy levels as: 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 4*s*, 3*d*, 4*p*, 5*s*, 4*d*, 5*p*, 6*s*, 4*f*, 5*d*, 6*p*, 7*s*, etc.

The (*n* + *l*) rule:

1. Higher the value of $(n + l)$ for a given orbital, greater is it's energy. For example, 4*s* $(n + l = 4 + 0 = 4)$ is has higher energy than 3*s* $(n + l = 3 + 0 = 3)$
2. If $(n + l)$ value for two orbitals are same, then the orbital with higher value of *n* will have higher energy. For example 4*s* $(n + l = 4 + 0 = 4)$ and 3*p* $(n + l = 3 + 1 = 4)$ have same $(n + l)$ values, therefore 4*s* will have higher energy than 3*p* orbital due to higher value of *n*.

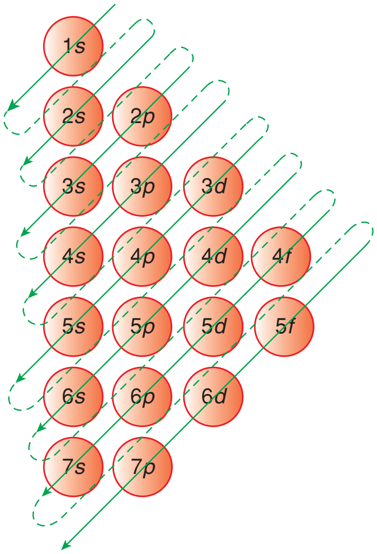


Figure 5.40 Sequence of filling energy levels.

Hund's Rule of Maximum Multiplicity

Hund's rule states that where orbitals are available in degenerate sets, maximum multiplicity is preserved; that is, electrons are not paired until each orbital in a degenerate set has been half-filled. This is an empirical rule that determines the lowest energy arrangement of electrons in a subshell. It implies that pairing of electrons in orbitals of *p*, *d* and *f* subshells does not take place till each orbital belonging to that subshell has got one electron each.

Note: Since there are three *p*, five *d* and seven *f* orbitals, the pairing of electrons in them would begin with the 4th, 6th and 8th electron, respectively. This is because half-filled and completely filled states are associated with extra stability.

Pauli's Exclusion Principle

Three quantum numbers *n*, *l* and m_l are needed to define an orbital. Each orbital may hold up to two electrons, provided they have opposite spins. An extra quantum number is required to define the spin of an electron in an orbital. Thus, four quantum numbers are needed to define the energy of an electron in an atom. **The Pauli exclusion principle states that no two electrons in one atom can have all four quantum numbers the same**. By permutating the quantum numbers, the maximum number of electrons which can be contained in each main energy level can be calculated.

Subshell	Number of Orbitals	Maximum Number of Electrons
s	1	2
p	3	6
d	5	10
f	7	14

The maximum electron population per shell is shown below.

Shell	Subshell	Maximum	Shell Population
1	1*s*	2	2
2	2*s* 2*p*	8	(2 + 6)
3	3*s* 3*p* 3*d*	18	(2 + 6 + 10)
4	4*s* 4*p* 4*d* 4*f*	32	(2 + 6 + 10 + 14)

This trend shows that the maximum electron population of a shell is $2n^2$.

Writing Electronic Configuration

Electronic configuration of atoms is the distribution of electrons into atomic orbitals. When atoms are in their ground state, the electrons occupy the lowest possible energy levels (Fig. 5.41).

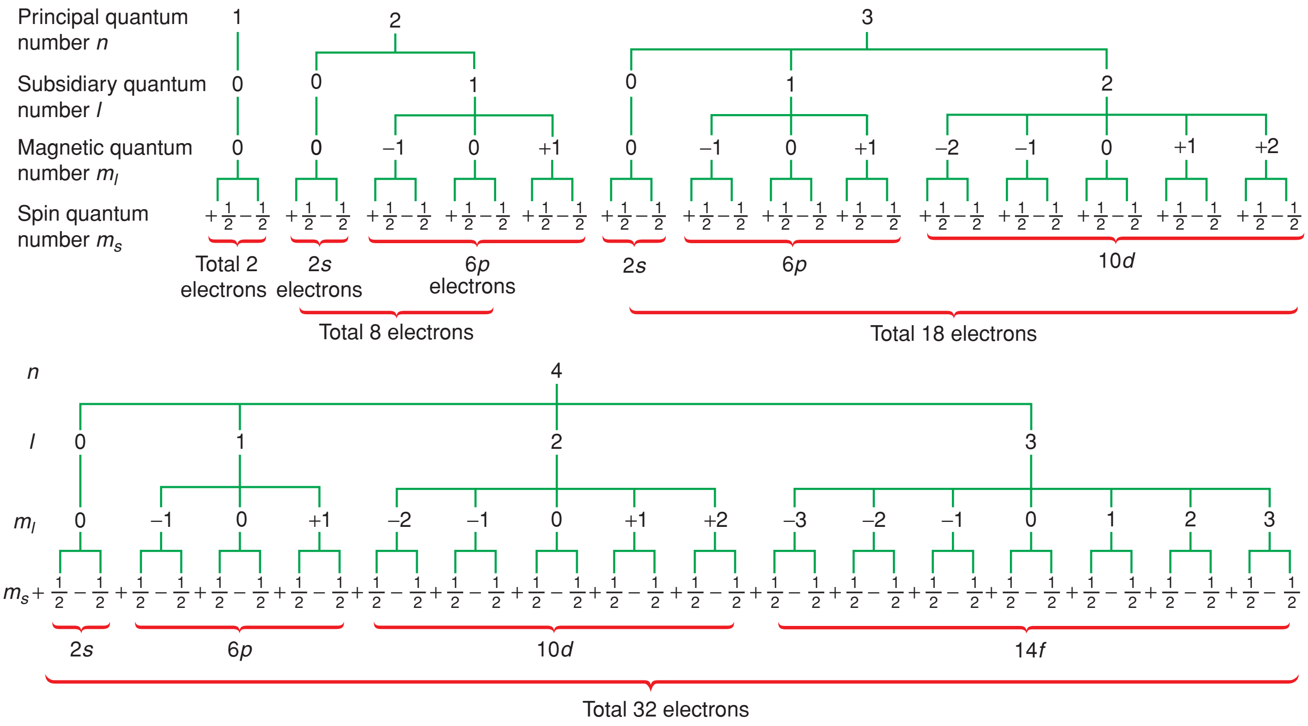


Figure 5.41 Quantum numbers, the permissible number of electrons and the shape of the periodic table.

To show the positions of the electrons in an atom, the symbols 1*s*, 2*s*, 2*p*, etc. are used to denote the main energy level and sublevel. A superscript indicates the number of electrons in each set of orbitals. Thus for hydrogen, the 1*s* orbital contains one electron, and this is shown as $1s^1$. For helium, the 1*s* orbital contains two electrons, denoted $1s^2$. The electronic structures of the first few atoms in the periodic table may be written as shown.

H	$1s^1$			
He	$1s^2$			End of Period 1 of the Periodic table.
Li	$1s^2$	$2s^1$		
Be	$1s^2$	$2s^2$		
B	$1s^2$	$2s^2$	$2p^1$	
C	$1s^2$	$2s^2$	$2p^2$	
N	$1s^2$	$2s^2$	$2p^3$	
O	$1s^2$	$2s^2$	$2p^4$	
F	$1s^2$	$2s^2$	$2p^5$	
Ne	$1s^2$	$2s^2$	$2p^6$	End of Period 2 of the Periodic table.
Na	$1s^2$	$2s^2$	$2p^6$	$3s^1$

An alternative way of showing the electronic structure of an atom is to draw boxes for orbitals, and arrows for the electrons (Fig. 5.42). By convention, electron spins are represented by arrows pointing up (↑) or down (↓). The orbital diagram for electronic configuration is more beneficial as all the four quantum numbers are represented by it.

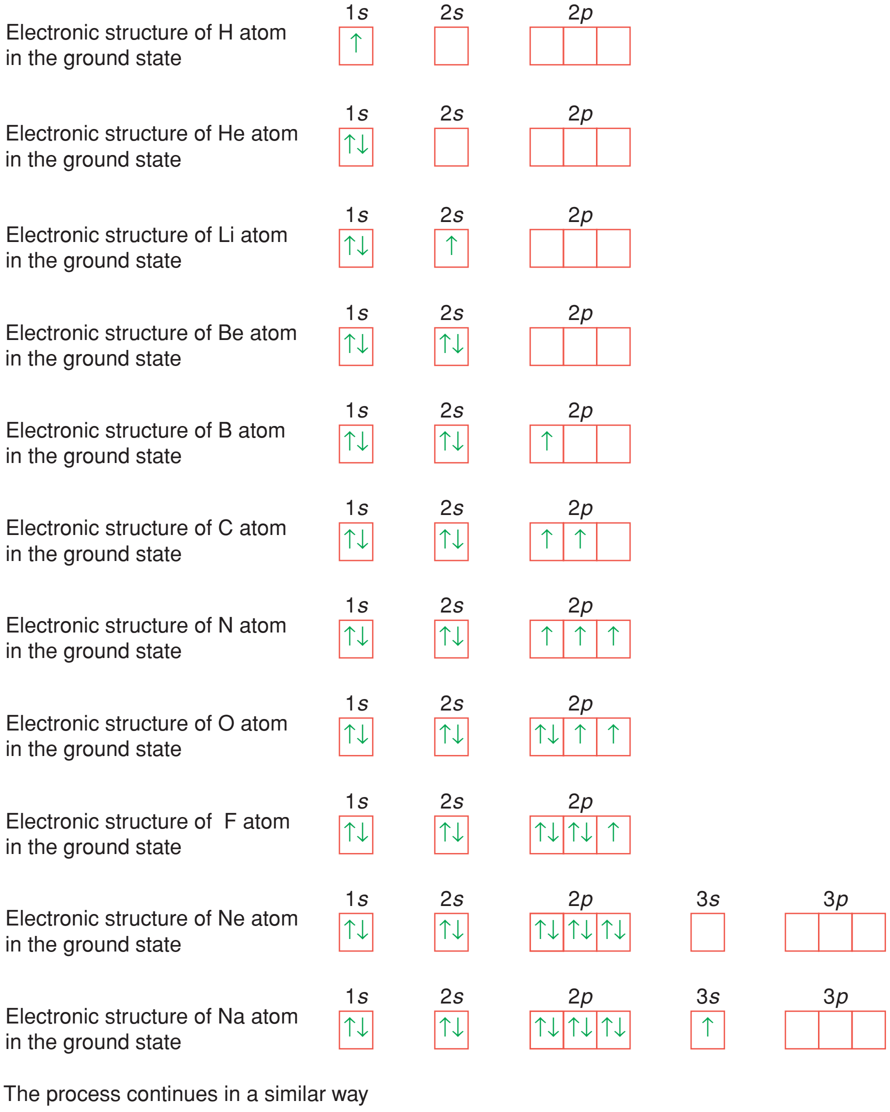

Electronic structure of H atom in the ground state
1s 2s 2p
↑
Electronic structure of He atom in the ground state
1s 2s 2p
↑↓
Electronic structure of Li atom in the ground state
1s 2s 2p
↑↓ ↑
Electronic structure of Be atom in the ground state
1s 2s 2p
↑↓ ↑↓
Electronic structure of B atom in the ground state
1s 2s 2p
↑↓ ↑↓ ↑
Electronic structure of C atom in the ground state
1s 2s 2p
↑↓ ↑↓ ↑ ↑
Electronic structure of N atom in the ground state
1s 2s 2p
↑↓ ↑↓ ↑ ↑ ↑
Electronic structure of O atom in the ground state
1s 2s 2p
↑↓ ↑↓ ↑↓ ↑ ↑
Electronic structure of F atom in the ground state
1s 2s 2p
↑↓ ↑↓ ↑↓ ↑↓ ↑
Electronic structure of Ne atom in the ground state
1s 2s 2p 3s 3p
↑↓ ↑↓ ↑↓ ↑↓ ↑↓
Electronic structure of Na atom in the ground state
1s 2s 2p 3s 3p
↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑
The process continues in a similar way

Figure 5.42 Alternate representation for electronic structure of an atom.

After the 1*s*, 2*s*, 2*p*, 3*s* and 3*p* levels have been filled at argon, the next two electrons go into the 4*s* level. This gives the elements potassium and calcium. Once the 4*s* level is full the 3*d* level is the next lowest in energy, not the 3*p* level. Thus the 3*d* starts to fill at scandium. The elements from scandium to copper (Note: Cr and Cu have only one electron in the 4*s* orbital.) have two electrons in the 4*s* level and an incomplete 3*d* level, and all behave in a similar manner chemically. Such a series of atoms is known as a **transition series**. A second transition series starts after the 5*s* orbital has been filled, at strontium, because in the next element, yttrium, the 4*d* level begins to fill up. A third transition series starts at lanthanum where the electrons start to fill the 5*d* level after the 6*d* level has been filled with two electrons.

A further complication arises here because after lanthanum, which has one electron in the 5*d* level, the 4*f* level begins to fill, giving the elements from cerium to lutetium with from one to 14*f* electrons. These are sometimes called the **inner transition elements**, but are usually known as the **lanthanoids** or **rare earth metals**.

When we consider the chemical reactions of atoms, our attention is usually focused on the distribution of electrons in the **outer shell** or the **valence shell** of the atom (the occupied shell with the largest value of *n*). This is because the **valence electrons** (those in the outer shell) are the ones that are exposed to other atoms when the atoms react. The inner electrons of an atom, called the **core electrons**, are buried deep within the atom and normally do not play a role when chemical bonds are formed.

Because we are interested primarily in the electrons of the outer shell, we often write electron configurations in an abbreviated or shorthand form. To write the *shorthand configuration* for an element we indicate what the core is by placing in brackets the symbol of the noble gas whose electron configuration is the same as the core configuration. This is followed by the configuration of the outer electrons for the particular element. Thus, for sodium and magnesium we write

$$\text{Na: } 1s^2\,2s^2\,2p^6\,3s^1 \qquad \text{Mg: } 1s^2\,2s^2\,2p^6\,3s^2$$

$$\text{Na: [Ne] } 3s^1 \qquad \text{Mg: [Ne] } 3s^2$$

Even with the transition elements, we need only concern ourselves with the outermost shell and the *d* subshell just below. For example, for iron with the configuration

$$\text{Fe: } 1s^2\,2s^2\,2p^6\,3s^3\,3p^6\,3d^6\,4s^2$$

The abbreviated configuration is written as

$$\text{Fe: [Ar] } 3d^6\,4s^2$$

Solved Example 5-57

Which of the following orbital diagrams is excluded by the Aufbau principle? Which by the Pauli exclusion principle? Which by Hund's rule? Which is correct? Explain how a principle or rule is violated in the others.

	1*s*	2*s*	2*p*		
(a)	↓↑	↑↓	↑↓	↑	
(b)	↓↑	↑↓	↑	↑	↑
(c)	↓↑	↑	↑↓	↑	↑
(d)	↓↑	↑↑	↑	↑	↑

Solution

(a) This is excluded by Hund's rule since electrons are not shown in separate orbitals of the same subshell with parallel spins.

(b) This is correct.

(c) This is excluded by the Aufbau principle because the 2*s* subshell fills before the 2*p*.

(d) This is excluded by the Pauli exclusion principle since the two electrons in the 2*s* orbital cannot have the same spin.

Solved Example 5-58

Give the sequence in which the energy levels in an atom are filled with electrons. Write the electronic configurations for the elements of atomic number 6, 11, 17 and 25, and from this decide to which group in the periodic table each element belongs.

Solution

The sequence is $1s\ 2s\ 2p\ 3s\ 3p\ 4s\ 3d\ 4p\ 5s\ 4d\ 5p\ 6s\ 4f\ 5d\ 6p\ 7s\ 5f\ 6d\ 7p\ldots$

Atomic number 6: $1s^2 2s^2 2p^2$ Group number = 4 + 10 = 14

Atomic number 11: $1s^2 2s^2 2p^6 3s^1$ Group number = 1

Atomic number 17: $1s^2 2s^2 2p^6 3s^2 3p^5$ Group number = 17

Atomic number 25: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$ Group number = 5

Explanation for Exceptions in Electronic Configuration in Cu and Cr

The rules that we have learnt for predicting electron configurations work most of the time, but not always. However, determined electronic configuration of atoms reveals that there are quite a few exceptions to the rules. For example, two important exceptions are for chromium and copper. Following the rules, we would expect the configurations to be

$$\text{Cr: [Ar]}\ 3d^4\ 4s^2 \qquad \text{Cu: [Ar]}\ 3d^9\ 4s^2$$

However, the actual electron configurations, determined experimentally, are

$$\text{Cr: [Ar]}\ 3d^5\ 4s^1 \qquad \text{Cu: [Ar]}\ 3d^{10}\ 4s^1$$

For chromium, an electron is "borrowed" from the $4s$ subshell to give a $3d$ subshell that is exactly half-filled. For copper the $4s$ electron is borrowed to give a completely filled $3d$ subshell. A similar thing happens with silver and gold, which have filled $4d$ and $5d$ subshells, respectively.

$$\text{Ag: [Kr]}\ 4d^{10}\ 5s^1 \qquad \text{Au: [Xe]}\ 4f^{14}\ 5d^{10}\ 6s^1$$

Apparently, half-filled and completely filled subshells (particularly the latter) have some special stability that makes such borrowing energetically favorable. Similar irregularities occur among the lanthanoid and the actinoid elements.

The stability of half-filled and completely filled subshells can be attributed to the following two reasons:

1. The half-filled and completely filled shells have symmetrical distribution of electrons, and therefore, are more stable as symmetry is associated with greater stability.
2. When two or more electrons are present in degenerate orbitals of a subshell with the same spin, they tend to exchange their positions. The energy released during this exchange is known as exchange energy. Electronic configurations with half-filled shells permit maximum number of exchanges between electrons of same spin, and thus maximum exchange energy is released which contributes to the stability of the state.
3. In case of Cu, the exchange energy is the same in both the cases. Thus, the stability achieved due to fully-filled and half-filled symmetrical distribution is the main criterion for the exceptional configuration of Cu.

Solved Example 5-59

In each of the following pairs of salts, which one is more stable?

(a) Ferrous and ferric salts

(b) Cuprous and cupric salts.

Solution

(a) **Ferrous and ferric salts:** In ferrous salts Fe^{2+}, the configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$. In ferric salts Fe^{3+}, the configuration is $1s^2 2s^2 2p^6 3s^3 3p^6 3d^5$. As half-filled $3d^5$ configuration is more stable, therefore, ferric salts are more stable than ferrous salts.

(b) **Cuprous and cupric salts:** In cuprous salts, the configuration of $Cu^+ = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$. In cupric salts, the configuration of $Cu^{2+} = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$. Although Cu^+ has completely filled d orbital, yet cuprous salts are less stable. This is because the nuclear charge is not sufficient enough to hold 18 electrons of Cu^+ ion present in the outermost shell.

Solved Example 5-60

Mo atom in its ground state has a $4d^5\ 5s^1$ configuration and Ag atom $4d^{10}\ 5s^1$ configuration. Explain why.

Solution

The extra stability of half and fully-filled electronic configurations can be explained in terms of symmetry and exchange energy. The half-filled and fully-filled electronic configurations have symmetrical distribution of electrons and this symmetry leads to stability. Moreover, in such configurations electrons can exchange their positions among themselves to maximum extent. This exchange leads to stabilization which is expressed in terms of exchange energy.

5.19 | MAGNETIC PROPERTIES

The spin magnetic moment is expressed as

$$\mu_s = \sqrt{4m_s(m_s+1)}$$

Substituting $m_s = (1/2)\,n$, we get the pin only formula as

$$\mu_s = \sqrt{n(n+2)}$$

where n is the number of unpaired electrons and the magnetic moment is expressed in Bohr Magneton. The magnetic moment (μ) can be measured from spin-only formula, which assumes that the magnetic moment arises entirely from the unpaired electron spin. This formula works reasonably well when there is not a significant contribution from the angular orbital moment along with the spin motion. If the species has unpaired electrons, it is **paramagnetic** and if all the electrons are paired, it is said to **diamagnetic**.

Relation of Colour with Paramagnetic and Diamagnetic Species

Usually, the paramagnetic species have unpaired electrons which can make transitions and at times these transitions fall into the visible spectra. Thus paramagnetic species usually have colour but it is not true always.

Similarly, diamagnetic species are usually colourless, but this is also not true always.

Solved Example 5-61

Which of the following ions has the highest magnetic moment: **(a)** Fe^{2+}, **(b)** Mn^{2+}, **(c)** Cr^{3+}, **(d)** V^{3+}.

Solution

The magnetic moment, $\mu = \sqrt{n(n+2)}$ where n = number of unpaired electrons.

(a) The configuration of Fe^{2+} is $3d^6$ ↑↓ ↑ ↑ ↑ ↑

↑↓ ↑ ↑ ↑ ↑

Therefore, $n = 4$ and magnetic moment is $\mu = \sqrt{4(4+2)} = 4.89$ BM

Solved Example 5-62

In which of the following options do both constituents of the pair have the same magnetic moment?

(a) Zn^{2+} and Cu^{2+} **(b)** Co^{2+} and Ni^{2+}

(c) Mn^{4+} and Co^{2+} **(d)** Mg^{2+} and Sc^{+}

Solution

(c) The electronic configuration of Mn^{4+} is d^3 ↑ ↑ ↑ ☐ ☐. Therefore, $n = 3$.

The electronic configuration of Co^{2+} is d^7 ↑↓ ↑↓ ↑ ↑ ↑. Therefore, $n = 3$.

Hence, magnetic moment is same for both, and is $\mu = \sqrt{3(3+2)} = 3.872$ BM

SOLVED OBJECTIVE QUESTIONS FROM PREVIOUS YEAR PAPERS

1. Which hydrogen-like species will have same radius as that of Bohr orbit of hydrogen atom?

(A) $n = 2, \text{Li}^{2+}$ (B) $n = 2, \text{Be}^{3+}$
(C) $n = 2, \text{He}^{+}$ (D) $n = 3, \text{Li}^{2+}$

(IIT-JEE 2004)

Solution

(B) The radius of the hydrogen-like species is calculated and compared with that of hydrogen.

$$r_n = \frac{0.529\ n^2}{Z}\ \text{Å}$$

$$r_1(\text{H}) = \frac{0.529 \times 1^2}{1} = 0.529\ \text{Å}$$

$$r_2(\text{Be}^{3+}) = \frac{0.529 \times 2^2}{4} = 0.529\ \text{Å}$$

2. The number of radial nodes in 3p and 4s orbitals, respectively, are

(A) 1, 3 (B) 3, 1
(C) 2, 2 (D) 2, 1

(IIT-JEE 2005)

Solution

(A) The number of radial nodes = $n - l - 1$. Now, for 3p, $n = 3, l = 1$. Substituting, we get

$$n - l - 1 = 3 - 1 - 1 = 1$$

For 4s, $n = 4, l = 0$. Substituting, we get

$$n - l - 1 = 4 - 0 - 1 = 3$$

3. According to Bohr's theory, E_n = total energy; K_n = kinetic energy; V_n = potential energy; R_n = radius of nth orbit. Match the following **(IIT-JEE 2006 Main)**

Column I		Column II	
(A)	$V_n/K_n = ?$	(p)	0
(B)	If radius of nth orbit $\propto E_n^x$ where $x = ?$	(q)	-1
(C)	Angular momentum in lowest orbital	(r)	-2
(D)	$\frac{1}{r^n} \propto Z^y, y = ?$	(s)	1

Solution

A → (r); B → (q); C → (p); D → (s)

Potential energy = $-Ze^2/r$ and kinetic energy = $Ze^2/2r$. Dividing the two, we get $V_n/K_n = -2$.
Total energy $= -Ze^2/2r$ or $r_n \propto E^{-1}$
Angular momentum = $nh/2\pi$. For $n = 0$, angular momentum is zero.
From the expression $r_n = a_0 n^2/Z$, therefore, $r_n \propto Z^{-1}$

4. Match the entries in Column I with the correctly related quantum number(s) in Column II. **(IIT-JEE 2008)**

Column I		Column II	
(A)	Orbital angular momentum of the electron in a hydrogen-like atomic orbital	(p)	Principal quantum number
(B)	A hydrogen-like one-electron wave function obeying Pauli principle	(q)	Azimuthal quantum number
(C)	Shape, size and orientation of hydrogen like atomic orbitals	(r)	Magnetic quantum number
(D)	Probability density of electron at the nucleus in hydrogen-like atom	(s)	Electron spin quantum number

Solution

A → (q); B → (s); C → (p, q, r); D → (p, q, r)

Azimuthal quantum number determines the orbital angular momentum of electron. It also determines the number determines the shape of the orbital
Pauli's exclusion principle states that an orbital can contain maximum of two electrons.
Principal quantum number determines the size of the orbital.
Magnetic quantum number determines the orientation of the orbital.
Three of the quantum number (principal, azimuthal, magnetic) together represents the probability density of electron.

5. Assuming that Hund's rule is violated, the bond order and magnetic nature of the diatomic molecule B_2 is

(A) 1 and diamagnetic (B) 0 and diamagnetic
(C) 1 and paramagnetic (D) 0 and paramagnetic

(IIT-JEE 2010)

Solution

(A) $\text{B}_2(10) = \sigma 1s^2\ \sigma^* 1s^2\ \sigma 2s^2\ \sigma^* 2s^2\ \pi 2px^2$. The bond order is $(6 - 4)/2 = 1$ and the nature is diamagnetic as there are no unpaired electron.

6. Read the paragraph, and answer the questions that follow:
The hydrogen-like species Li^{2+} is in a spherically symmetric state S_1 with one radial node. Upon absorbing light, the ion undergoes transition to a state S_2. The state S_2 has radial node and its energy is equal to the ground state energy of the hydrogen atom.

6a. The state S_1 is **(IIT-JEE 2010)**

(A) 1s (B) 2s
(C) 2p (D) 3s

Solution

(B) For S_1 (spherically symmetrical), node = 1, or $n - 1 = 1$
$\Rightarrow n = 2$
For S_2, radial node = 1, so

$$E_{S_2} = -13.6 \times \frac{Z^2}{n^2} = E_H \text{ in ground state} = -13.6$$

or

$$E = -13.6 \times \frac{9}{n^2} \quad \Rightarrow n = 3$$

So, the state in S_1 is 2*s* and S_2 is 3*p*

6b. Energy of the S_1 in units of the hydrogen atom ground state energy is
(A) 0.75 (B) 1.50
(C) 2.25 (D) 4.50

Solution

(C) The relations between energy in S_1 state and that of ground state of hydrogen atom is

$$\frac{E_{S_1}}{E_H} = \frac{-13.6 \times 9}{4 \times (-13.6)} = 2.25$$

6c. The orbital angular momentum quantum number of the state S_2 is
(A) 0 (B) 1
(C) 2 (D) 3

Solution

(B) Azimuthal quantum number for $S_2 = 1$

7. The maximum number of electrons that can have principal quantum number, $n = 3$, a spin quantum number, $m_s = -(1/2)$ is __________. **(IIT-JEE 2011)**

Solution

(9) For $n = 3$, the total number of orbitals = $n^2 = 9$. This means 18 electrons can be accommodated in 9 orbitals in which 9 will have spin clockwise ($m_s = +1/2$) and 9 will have anticlockwise ($m_s = -1/2$).

8. The kinetic energy of an electron in the second Bohr orbit of a hydrogen atom is (a_0 is the Bohr radius).

(A) $\dfrac{h^2}{4\pi^2 m a_0^2}$ (B) $\dfrac{h^2}{16\pi^2 m a_0^2}$

(C) $\dfrac{h^2}{32\pi^2 m a_0^2}$ (D) $\dfrac{h^2}{64\pi^2 m a_0^2}$

(IIT-JEE 2012)

Solution

(C) According to Bohr's postulate, the angular momentum of an electron is quantized, that is,

$$mvr = \frac{nh}{2\pi} \quad \Rightarrow v = \frac{nh}{2\pi mr}$$

Now, substituting the above expression in the kinetic energy expression (1/2) mv^2, we get

$$\text{K.E.} = \frac{1}{2} m \left(\frac{nh}{2\pi mr} \right)^2 \qquad (1)$$

where *r* is the radius of Bohr's orbit, that is, $r = a_0 \times n^2/Z$. For the second Bohr's orbit of a hydrogen atom, substituting $Z = 1$ and $n = 2$, we get $r = 4a_0$ where a_0 is a constant. Now, substituting this value of *r* in Eq. (1), we get

$$\text{K.E.} = \frac{1}{2} \times m \left(\frac{4h^2}{4\pi^2 m^2 \cdot 16 a_0^2} \right) = \frac{h^2}{32\pi^2 m a_0^2}$$

9. Assuming that Hund's rule is violated, the bond order and magnetic nature of the diatomic molecule B_2 is
(A) 1 and diamagnetic. (B) 0 and diamagnetic.
(C) 1 and paramagnetic. (D) 0 and paramagnetic.
(IIT-JEE 2010)

Solution

(A) The configuration of B_2 is

$$B_2(10) = \sigma 1s^2 \ \sigma^* 1s^2 \ \sigma 2s^2 \ \sigma^* 2s^2 \ \pi 2px^2$$

Therefore, bond order is $= \dfrac{6-4}{2} = 1.$

So, the nature is diamagnetic as there are no unpaired electrons.

10. The work function (W_0) of some metals is listed below. The number of metals which will show photoelectric effect when light of 300 nm wavelength falls on the metal is __________. **(IIT-JEE 2011)**

Metal	Li	Na	K	Mg	Cu	Ag	Fe	Pt	W
W_0 (eV)	2.4	2.3	2.2	3.7	4.8	4.3	4.7	6.3	4.75

Solution

(4) Given that wavelength is $\lambda = 300$ nm $= 300 \times 10^{-9}$ m $= 3 \times 10^{-7}$ m. Therefore, energy is

$$E = h\nu = \frac{hc}{\lambda} = \frac{6.6 \times 10^{-34} \times 3 \times 10^8}{3 \times 10^{-7}}$$

$$= 6.6 \times 10^{-19}\,\text{J} = \frac{6.6 \times 10^{-19}}{1.6 \times 10^{-19}} = 4.1\,\text{eV}$$

For a metal to show photoelectric effect, its work function has to be less than or equal to 4.1 eV. So, the number of metals having work function less than 4.1 eV are Li, Na, K and Mg.

11. The atomic masses of He and Ne are 4 and 20 amu, respectively. The value of the de Broglie wavelength of He gas at −73°C is *M* times that of the de Broglie wavelength of Ne at 727°C. *M* is __________. **(JEE Advanced 2013)**

Solution

(5) We know that $\lambda = \dfrac{h}{\sqrt{2mE}}$,

where E (kinetic energy) $\propto T$.

Therefore, $\lambda \propto \dfrac{h}{\sqrt{mT}}$

$$\frac{\lambda_{\text{He}}}{\lambda_{\text{Ne}}} = \frac{h/\sqrt{m_{\text{He}}T_{\text{He}}}}{h/\sqrt{m_{\text{Ne}}T_{\text{Ne}}}} = \sqrt{\frac{m_{\text{Ne}}T_{\text{Ne}}}{m_{\text{He}}T_{\text{He}}}} = \sqrt{\frac{20\times 1000}{4\times 200}} = 5$$

12. In an atom, the total number of electrons having quantum numbers $n = 4$, $|m_l| = 1$ and $m_s = -1/2$ is __________. **(JEE Advanced 2014)**

Solution

(6) As $n = 4$, so $l = 0, 1, 2, 3$ which implies the orbitals are 4s, 4p, 4d and 4f.
Now, $|m_l| = 1$ implies $m_l = +1$ and -1. Therefore, l can be 3, 2, 1, as for $l = 0$, $m_l = 0$.T
For $l = 1$, $m_l = -1, 0, +1$
For $l = 2$, $m_l = -2, -1, 0, +1, +2$
For $l = 3$, $m_l = -3, -2, -1, 0, +1, +2, +3$
Therefore, there are six possible orbitals with $|m_l| = 1$.
Also, given that $m_s = -1/2$ so six electrons are possible with $m_s = -1/2$.

13. Not considering the electronic spin, the degeneracy of the second excited state ($n = 3$) of H atom is 9, while the degeneracy of the second excited state of H$^-$ is __________. **(JEE Advanced 2015)**

Solution

(3) H atom is a single electron system whereas H$^-$ is a multi-electron system. Orbitals 2s, 2p differ in energy in multi-electron system; 2s < 2p.
In the first excited state, electron moves from 1s to 2s.
In the second excited state, electron moves from 1s to 2p.
So, the degeneracy of second excited state 2p = 3.

14. In Bohr series of lines hydrogen spectrum, the third line from the red end corresponds to which one of the following inter-orbit jumps of the electron for Bohr orbits in an atom of hydrogen?

(A) $3 \rightarrow 2$ (B) $5 \rightarrow 2$
(C) $4 \rightarrow 1$ (D) $2 \rightarrow 5$ **(AIEEE 2003)**

Solution

(B) Line from the red end belongs to Balmer series for which $n_1 = 2$ and $n_2 = 3, 4, 5$ for first second and third line.

15. The de Broglie wavelength of a tennis ball of mass 60 g moving with a velocity of 10 m s^{-1} is approximately [Planck's constant = 6.63×10^{-34} J s]

(A) 10^{-33} m (B) 10^{-31} m
(C) 10^{-16} m (D) 10^{-25} m **(AIEEE 2003)**

Solution

(A) According to de Broglie relationship,

$$\lambda = \frac{h}{mv} = \frac{6.63\times 10^{-34}}{60\times 10^{-3}\times 10} = 1.105\times 10^{-33}\ \text{m}$$

16. The orbital angular momentum for an electron revolving in an orbit is given by $l(l+1)\times(h/2p)$. This momentum for an s electron will be given by

(A) $+1/2(h/2\pi)$ (B) 0
(C) $(h/2\pi)$ (D) $2(h/2\pi)$
(AIEEE 2003)

Solution

(B) This is because for s orbital, $l = 0$.

17. Which of the following sets of quantum numbers is correct for an electron in 4f orbital?

(A) $n = 4, l = 3, m = +4, s = +(1/2)$
(B) $n = 3, l = 2, m = -2, s = +(1/2)$
(C) $n = 4, l = 3, m = +1, s = +(1/2)$
(D) $n = 4, l = 4, m = -4, s = -(1/2)$ **(AIEEE 2004)**

Solution

(C) When $n = 4, l = 3, m = +1, s = +(1/2)$ as $l = n - 1$, $m = -l$ to $+l$ and $s = +1/2$ or $-1/2$.

18. Consider the ground state of Cr atom ($Z = 24$). The number of electrons with the azimuthal quantum numbers $l = 1$ and 2 are, respectively,

(A) 12 and 4 (B) 16 and 5
(C) 16 and 4 (D) 12 and 5
(AIEEE 2004)

Solution

(D) 12 and 5. The configuration of Cr is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^5$
For $l = 1$, $p = 6 + 6 = 12$ and for $l = 2$, $d = 5$.

19. The wavelength of the radiation emitted, when in hydrogen atom electron falls from infinity to stationary state 1, would be (Rydberg constant = 1.097×10^7 m^{-1})

(A) 91 nm (B) 9.1×10^{-8} nm
(C) 406 nm (D) 192 nm **(AIEEE 2004)**

Solution

(A) Using the formula,

$$\frac{1}{\lambda} = R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

Substituting n_2 = infinity (given) and $n_1 = 1$, we get

$$\frac{1}{\lambda} = 1.097\times 10^7 \times [1]$$

or $$\lambda = \frac{1}{1.097\times 10^7} = 91\ \text{nm}$$

20. In a multi-electron atom, which of the following orbitals described by the three quantum number will have the same energy in the absence of magnetic and electric fields? **(AIEEE 2005)**

(I) $n = 1, l = 0, m = 0$ (II) $n = 2, l = 0, m = 0$
(III) $n = 2, l = 1, m = 1$ (IV) $n = 3, l = 2, m = 0$
(V) $n = 3, l = 2, m = 0$

(A) I and II
(B) II and III
(C) III and IV
(D) IV and V

Solution

(D) This is because the energy levels follow $n + l$ rule and the values are same for IV and V, that is, 3 + 2 = 5 for both the levels.

21. According to Bohr's theory, the angular momentum of an electron in 5th orbit is

(A) $25h/\pi$
(B) $1.0h/\pi$
(C) $10h/\pi$
(D) $mvr = nh$

(AIEEE 2006)

Solution

(D) According to Bohr's postulate of quantization of angular momentum, the angular momentum of an electron should be an integral multiple of $h/2\pi$, that is,

$$mvr = \frac{nh}{2\pi}$$

Since $n = 5$, we get

$$mvr = \frac{5h}{2\pi} = \frac{2.5h}{\pi}$$

22. Uncertainty in the position of an electron (mass = 9.1 × 10^{-31} kg) moving with a velocity 300 m s^{-1}, accurate upto 0.001%, will be (where $h = 6.63 \times 10^{-34}$ J s)

(A) 19.2×10^{-2} m
(B) 5.76×10^{-2} m
(C) 1.92×10^{-2} m
(D) 3.84×10^{-2} m

(AIEEE 2006)

Solution

(C) According to Heisenberg uncertainty principle,

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi} \quad \text{or} \quad \Delta p = m\Delta v \quad \text{or} \quad \Delta x \geq \frac{h}{4\pi m \Delta v}$$

Also, $\Delta v = 0.001\%$ of 300. Substituting, we get

$$\Delta x = \frac{6.63 \times 10^{-34}}{4 \times 3.14 \times 9.1 \times 10^{-31} \times 300 \times \dfrac{0.001}{100}} = 0.01933 \text{ m}$$

or $\Delta x = 1.93 \times 10^{-2}$ m.

23. Which of the following sets of quantum numbers represents the highest energy of an atom?

(A) $n = 3, l = 0, m = 0, s = +1/2$
(B) $n = 3, l = 1, m = 1, s = +1/2$
(C) $n = 3, l = 2, m = 1, s = +1/2$
(D) $n = 4, l = 0, m = 0, s = +1/2$

(AIEEE 2007)

Solution

(C) According to $(n + l)$ rule, more is the value of $(n + l)$ more is the energy. Hence, when $n = 3$ and $l = 2$, then $(n + l) = (3 + 2) = 5$.

24. Which one of the following constitutes a group of the isoelectronic species?

(A) C_2^{2-}, O_2^{2-}, CO, NO
(B) NO^+, C_2^{2-}, CN^-, N_2
(C) CN^-, N_2, O_2^{2-}, C_2^{2-}
(D) N_2, O_2^{2-}, NO^+, CO

(AIEEE 2008)

Solution

(B) The number of electrons in each species is

$$NO^+ = 7 + 8 - 1 = 14, C_2^{2-} = 6 + 6 + 2 = 14$$
$$CN^- = 6 + 7 + 1 = 14, N_2 = 7 \times 2 = 14$$

25. Calculate the wavelength (in nanometers) associated with a proton moving at 1.0 × 10^3 ms^{-1} (mass of proton = 1.67×10^{-27} kg and $h = 6.63 \times 10^{-34}$ J s).

(A) 0.032 nm
(B) 0.40 nm
(C) 2.5 nm
(D) 14.0 nm

(AIEEE 2009)

Solution

(B) Using de Broglie relationship

$$\lambda = \frac{h}{mv} = \frac{6.63 \times 10^{-34}}{1.67 \times 10^{-27} \times 10^3} = 0.40 \text{ nm}$$

26. The ionization enthalpy of hydrogen atom is 1.312 × 10^6 J mol^{-1}. The energy required to excite the electron in the atom from $n = 1$ to $n = 2$ is

(A) 8.51×10^5 J mol^{-1}
(B) 6.56×10^5 J mol^{-1}
(C) 7.56×10^5 J mol^{-1}
(D) 9.84×10^5 J mol^{-1}

(AIEEE 2008)

Solution

(D) The energy for stationary states $n = 1$ and $n = 2$ are, respectively,

$$E_1 = \frac{1.312 \times 10^6}{(1)^2} \quad \text{and} \quad E_2 = -\frac{1.312 \times 10^6}{(2)^2}$$

Therefore,

$$\Delta E = E_2 - E_1 = -\frac{1.312 \times 10^6}{2^2} - \left(-\frac{1.312 \times 10^6}{1}\right)$$
$$= 9.84 \times 10^5 \text{ J mol}^{-1}$$

27. In an atom, an electron is moving with a speed of 600 ms^{-1} with an accuracy of 0.005%. Certainty with which the position of the electron can be located is ($h = 6.6 \times 10^{-34}$ kg m^2 s^{-1}, mass of electron $m_e = 9.1 \times 10^{-31}$ kg)

(A) 1.52×10^{-4} m
(B) 5.10×10^{-3} m
(C) 1.92×10^{-3} m
(D) 3.84×10^{-3} m

(AIEEE 2009)

Solution

(C) Using Heisenberg's uncertainty principle,

$$\Delta x \cdot m\Delta v = \frac{h}{4\pi}$$

or

$$\Delta x = \frac{h}{4\pi m \Delta v}$$

Given that $\Delta v = 0.005\%$ of $600\ \text{m s}^{-1}$, so

$$\Delta v = 600 \times \frac{0.005}{100} = 0.03\ \text{m s}^{-1}$$

Hence,

$$\Delta x = \frac{6.6 \times 10^{-34}}{4 \times 3.14 \times 9.1 \times 10^{-31} \times 0.03} = 1.92 \times 10^{-3}\ \text{m}$$

28. The energy required to break one mole of Cl–Cl bonds in Cl_2 is 242 kJ mol^{-1}. The longest wavelength of light capable of breaking Cl–Cl bonds is ($c = 3 \times 10^8$ m s^{-1} and $N_A = 6.02 \times 10^{23}$ mol^{-1})

(A) 494 nm (B) 594 nm
(C) 640 nm (D) 700 nm **(AIEEE 2010)**

Solution

(A) Energy required to break Cl_2 molecule

$$= \frac{(242 \times 10^3)}{N_A}\ \text{J.}$$

From $\quad E = h\nu \quad \Rightarrow E = h\dfrac{c}{\lambda}$

we have

$$\lambda = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{E} = \frac{242 \times 10^3}{6.022 \times 10^{23}}$$

$$= 4947\ \text{Å} = 494.7\ \text{nm}$$

29. Ionization enthalpy of He is 19.6×10^{-18} J atom^{-1}. The enthalpy of the first transition state ($n = 1$) of Li^{2+} is

(A) 8.82×10^{-17} J atom^{-1} (B) 4.41×10^{-16} J atom^{-1}
(C) -4.41×10^{-17} J atom^{-1} (D) -2.2×10^{-15} J atom^{-1}
(AIEEE 2010)

Solution

(A) The expression for ionization enthalpy is

$$E_{He^+} = 13.6 Z^2_{He^+}\left[\frac{1}{1^2} - \frac{1}{\infty^2}\right] = 13.6 Z^2_{He^+}$$
$$= 19.6 \times 10^{-19} \quad (Z_{He^+} = 2)$$

(as ionization enthalpy of He is 19.6×10^{-18} J atom^{-1})

So, $\quad 13.6 \times Z^2_{He^+} = 19.6 \times 10^{-18}$ J atom^{-1} $\qquad$ (1)

$$(E_1)_{Li^{2+}} = -13.6\, Z^2_{Li^{2+}}\left[\frac{1}{1^2} - \frac{1}{\infty^2}\right]$$

Multiplying and dividing by $Z^2_{He^+}$, we get

$$(E_1)_{Li^{2+}} = -13.6\, Z^2_{Li^{2+}}\frac{Z^2_{He^+}}{Z^2_{He^+}}\left[\frac{1}{1^2}\right]$$
$$= -13.6\, Z^2_{He^+} \times \frac{9}{4} = -19.6 \times 10^{-18} \times \frac{9}{4} \quad \text{[From Eq. (1)]}$$
$$= -4.41 \times 10^{-7}\ \text{J atom}^{-1}$$

30. A gas absorbs a photon of 355 nm and emits at two wavelengths. If one of the emissions is at 680 nm, the other is at

(A) 325 nm (B) 743 nm
(C) 518 nm (D) 1035 nm **(AIEEE 2011)**

Solution

(B) From the relation

$$\frac{1}{\lambda_{\text{absorbed}}} = \frac{1}{\lambda_1} + \frac{1}{\lambda_2} \Rightarrow \frac{1}{355} = \frac{1}{680} + \frac{1}{\lambda_2}$$

Solving, we get $\lambda_2 = 743$ nm.

31. The electrons identified by quantum numbers n and l:

(I) $n = 4, l = 1$ (II) $n = 4, l = 0$
(III) $n = 3, l = 2$ (IV) $n = 3, l = 1$

can be placed in order of increasing energy as:

(A) (III) < (IV) < (II) < (I) (B) (IV) < (II) < (III) < (I)
(C) (II) < (IV) < (I) < (III) (D) (I) < (III) < (II) < (IV)
(AIEEE 2012)

Solution

(B) Using $n + l$ rule, that is, lower the $n + l$ value, lower will be its energy. In case $n + l$ value is the same, then the one having lower n value will be lower in energy.

(I) $n = 4, l = 1, n + 1 = 4 + 1 = 5$
(II) $n = 4, l = 0, n + 1 = 4 + 0 = 4$
(III) $n = 3, l = 2; n + 1 = 3 + 2 = 5$ (here the n value is lower).
(IV) $n = 3, l = 1; n + 1 = 3 + 1 = 4$ (here the n value is lower, so it is lower in energy). Thus, the order is IV < II < III < I.

32. The correct set of four quantum numbers for the valence electrons of rubidium atom ($Z = 37$) is

(A) $5, 0, 0, +\frac{1}{2}$ (B) $5, 1, 0, +\frac{1}{2}$
(C) $5, 1, 1, +\frac{1}{2}$ (D) $5, 0, 1, +\frac{1}{2}$
(JEE Main 2014)

Solution

(A) For Rb ($Z = 37$), the electronic configuration is $1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, 3d^{10}\, 4s^2\, 4p^6\, 5s^1$
As the last electron enters $5s$ orbital, $n = 5$, $l = 0$ and $m_l = 0$, and since only one electron is present in the s-orbital, $m_s = +1/2$.

33. Which of the following is the energy of a possible excited state of hydrogen?

(A) −6.8 eV (B) −3.4 eV
(C) +6.8 eV (D) +13.6 eV
(JEE Main 2015)

Solution

(B) Energy of hydrogen atom $E_n = -13.6 \times \dfrac{Z^2}{n^2}$ eV

where $Z = 1$ and $n = 2$. Substituting, we get

$$E = -13.6 \times \frac{1}{4} = -3.4\ \text{eV}$$

REVIEW QUESTIONS

1. Give the numbers of neutrons, protons, and electrons in the atoms of each of the following isotopes. **(a)** radium-226, **(b)** ^{206}Pb, **(c)** carbon-14, **(d)** ^{23}Na.

2. Which property of light waves is a measure of the brightness of the light? Which specifies the color of the light? Which is related to the energy of the light?

3. Explain in detail the findings of Thomson's model of the atom. What were the shortcomings?

4. According to Rutherford's model of the atom, where is the positive charge concentrated? What does it predict about the relative size of the nucleus and the radius of the atom? What is the nucleus composed of according to his model?

5. Where in an atom is nearly all of its mass concentrated? Explain your answer in terms of the particles that contribute to this mass.

6. Arrange the following regions of the electromagnetic spectrum in order of increasing wavelength (i.e., shortest wavelength → longest wavelength): microwaves, TV, X-rays, ultraviolet, visible, infrared, gamma rays.

7. What are the names used to refer to the theories that apply the matter–wave concept to electrons in atoms?

8. What is an atomic spectrum? How does it differ from a continuous spectrum? What fundamental fact is implied by the existence of atomic spectra?

9. In the spectrum of sodium, there is a line with a wavelength of 589 nm. **(a)** What color is this line? **(b)** What is its frequency? **(c)** What is the energy of each of its photons?

10. Consider the symbol ${}^{a}_{b}\text{X}$, where X stands for the chemical symbol for an element. What information is given in locations a and b?

11. What, if anything, is wrong with the following electron configurations for atoms in their ground states: **(a)** $1s^2 2s^1 2p^3$; **(b)** [Kr] $3d^7 4s^2$; **(c)** $1s^2 2s^2 2p^4$; **(d)** [Xe] $4f^{14} 5d^8 6s^1$?

12. Calculate the percentage of higher isotope of neon which has atomic mass 20.2 and the isotopes have the mass numbers 20 and 22.

13. When a copper atom loses an electron to become a Cu^+ ion, what are the possible quantum numbers of the electron that was lost?

14. The first shell may contain up to 2 electrons, the second shell up to 8, the third shell up to 18, and the fourth shell up to 32. Explain this arrangement in terms of quantum numbers.

15. What were the characteristics observed in the modified cathode ray experiment that led to the discovery of protons?

16. How does the behavior of very small particles differ from that of the larger, more massive objects that we meet in everyday life? Why don't we notice this same behavior for the larger, more massive objects?

17. **(a)** Name the first five series of lines that occur in the atomic spectrum of hydrogen and indicate the region in the electromagnetic spectrum where these series occur. **(c)** Give a general equation for the wave number applicable to all the series.

18. Give the notation for subshells denoted by the following quantum numbers: **(a)** $n = 6, l = 2$; **(b)** $n = 4, l = 3$; **(c)** $n = 4, l = 2$; **(d)** $n = 5, l = 4$.

19. How does the size of a given type of orbital vary with n?

20. On the basis of Heisenberg's principle, show why an electron cannot exist in the nucleus?

21. If a transition from an upper level to $n = 1$ in hydrogen spectrum results in light of wavelength 9.50×10^{-8} m in being emitted, what is the principal quantum number of the higher level?

22. Calculate the maximum number of electrons in the $n = 1$, $n = 2$, $n = 3$ and $n = 4$ shells.

23. State Heisenberg's uncertainty principle. What is the uncertainty in the position of a particle, if the uncertainty in the momentum is 10^{-11} kg m s^{-1}.

24. What is photoelectric effect? Calculate the frequency and energy of a photon of light with wavelength 520 nm.

25. The minimum energy required to eject an electron from a metal is 4.34×10^{-19} J. What is the minimum frequency of light required for photoelectric effect in the metal?

26. Give the names and symbols of the four quantum numbers required to define the energy of electrons in atoms. What do these quantum numbers relate to, and what numerical values are possible for each? Show how the shape of the periodic table is related to these quantum numbers.

27. Give the values of the four quantum numbers for each electron in the ground state for **(a)** the oxygen atom, and **(b)** the scandium atom. (Use positive values for m_l and m_s first.)

28. Which of the following species does the Bohr theory apply to? **(a)** H, **(b)** H^+, **(c)** He, **(d)** He^+, **(e)** Li, **(f)** Li^+, **(g)** Li^{+2}, **(h)** Be, **(g)** Be^+, **(h)** Be^{2+}, **(i)** Be^{3+}

29. How does the Bohr theory of the hydrogen atom differ from that of Schrödinger?

30. What is the order of uncertainty in momentum if the uncertainty in position of a particle is 10^{-34}?

31. Explain why the effect of Heisenberg uncertainty principle is only significant in case of microscopic particles and not in macroscopic objects.

32. Explain why three quantum numbers are required to describe an orbital. What feature of the three-dimensional structure of an orbital is specified by each of these quantum numbers?

33. Give two reasons why electrons tend to avoid each other.

34. Describe the relationship between the atomic number, mass number, number of protons, number of neutrons and number of electrons in a calcium atom, ^{40}Ca.

NUMERICAL PROBLEMS

1. Identify the element that has atoms with mass numbers of 20 that contain 11 neutrons.

2. The number of electrons, protons and neutrons in a species is equal to 10, 13 and 14, respectively. Assign the proper symbol to the species.

3. What is the range of frequencies of the waves used in a microwave oven?

4. Orchestras tune their instruments to the note "A", which has a frequency of 440 cycles s^{-1}, or 440 Hz. If the speed of sound is 340 m s^{-1}, what is the wavelength of this note?

5. The human ear is capable of hearing sound waves with frequencies between 20 and 20,000 Hz. If the speed of sound is 340.3 ms^{-1} at sea level, what is the wavelength in meters of the longest wave the human ear can hear?

6. The green line of barium atom emission has a wavelength of 554 nm. Calculate the frequency of this light and the energy of photon of this light.

7. The photoelectric work function for magnesium is 5.90×10^{-19} J. Calculate the minimum frequency of light required to eject electrons from the surface of magnesium. What is kinetic energy of the ejected electron when a light of wavelength 285 nm strikes the surface?

8. Calculate the frequency and the wavelength of the light emitted when the electron in hydrogen atom undergoes a transition from an orbit with $n = 5$ to $n = 3$.

9. An electron in the lithium atom is in the third energy level. Is the atom in the ground state or excited state? Can the atom emit light? If so, how?

10. The radius of an orbit is given by $r_n = 0.0529\ n^2$ (nm). Calculate the radius of the third orbit.

11. What is the distance of separation between second and third orbits of hydrogen atoms?

12. The ultraviolet emission line of magnesium is observed at 285 nm. What is the energy difference between the two levels responsible for this emission?

13. Calculate the wavelength (in nm) of an electron travelling with a speed of 2.79×10^6 m s^{-1}. (Mass of an electron is 9.11×10^{-31} kg.)

14. **(a)** The energy associated with the first orbit in the hydrogen atom is -2.18×10^{-18} J $atom^{-1}$. What is the energy associated with the fifth orbit?

(b) Calculate the radius of Bohr's fifth orbit for hydrogen atom.

15. The electron energy in hydrogen atom is given by $E = (-21.7 \times 10^{-12})/n^2$ ergs. Calculate the energy required to remove an electron completely from the $n = 2$ orbit. What is the longest wavelength (in cm) of light that can be used to cause this transition?

16. Calculate the number of electrons in a charged particle having a static electric charge of 7.25×10^{16} C.

17. In the visible spectrum, the wavelength of violet light is 450 nm and that of red light is 750 nm. Calculate the frequency and wavenumber of these radiations.

18. How many times heavier is a ^6Li atom than a ^1H atom?

19. Iodine molecule dissociates into after absorbing light of 4500 Å. If one quantum of radiation is absorbed by each molecule, calculate the kinetic energy of iodine atoms. (Bond energy of $I_2 = 240$ kJ mol^{-1}).

20. What is energy of a photon of light whose **(a)** wavelength is 400 nm and **(b)** frequency is 1300 kHz.

21. Calculate the frequency and the wavelength of the light emitted when the electron in a hydrogen atom undergoes a transition from an orbit with $n = 4$ to an orbit with $n = 2$.

22. If electromagnetic radiation with energy of 1166 kJ mol^{-1} was absorbed by a mole of hydrogen atoms in their lowest energy state, what would be the resulting energy of the hydrogen atoms? What would be the resulting energy level (i.e., what would be the value of n)?

23. Calculate the frequency and the wavelength of the light emitted when the electron in hydrogen atom undergoes a transition from an orbit with $n = 5$ to $n = 3$.

24. The $n = 8$ and $n = 9$ energy levels are very close in energy. Using the Bohr model, describe how the wavelengths of light compare as an electron falls from these two energy levels to the $n = 1$ energy level.

25. A microscope using suitable photons is employed to located an electron in an atom within a distance of 0.1 Å. What is the uncertainty involved in the measurement of its velocity?

26. Calculate the effective nuclear charge in 3p electron in silicon.

ADDITIONAL OBJECTIVE QUESTIONS

Single Correct Choice Type

1. During the emission spectrum, the first line of Lyman series of hydrogen atom occurs as $\lambda = x$ Å. The wave length of the first line of Lyman series of He$^+$ ion will occur at

(A) $4/x$
(B) $x/4$
(C) $3/x$
(D) $4x$

2. The quantum numbers of +1/2 and –1/2 for the electron spin represent

(A) rotation of the electron in clockwise and anticlockwise direction, respectively.

(B) rotation of the electron in anticlockwise and clockwise direction, respectively.

(C) magnetic moment of the electron pointing up and down, respectively.
(D) two quantum mechanical spin states which have no classical analog.

3. Which of the following describes an orbital
(A) ψ
(B) ψ^2
(C) $[\psi^2]\psi$
(D) None of these

4. The wave function (ψ) of 2*s* is given by:

$$\psi_{2x} = \frac{1}{2\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{1/2}\left\{2-\frac{r}{a_0}\right\}e^{-r/2a_0}$$

At $r = r_0$, radial node is formed. Thus for 2*s*, r_0 in terms of a_0 is:
(A) $r_0 = a_0$
(B) $r_0 = 2a_0$
(C) $r_0 = a_0/2$
(D) $r_0 = 4a_0$

5. Of the following transition in hydrogen atom, the one which gives an absorption line of maximum wavelength is
(A) $n = 1$ to $n = 2$
(B) $n = 3$ to $n = 8$
(C) $n = 2$ to $n = 1$
(D) $n = 8$ to $n = 3$

6. The probabilities of finding an electron residing in a p_x orbital is zero in the
(A) *yz* plane
(B) *xy* plane
(C) *xz* plane
(D) *y* and *z* directions

7. Maximum number of electrons in a subshell of an atom is determined by the following:
(A) $2n^2$
(B) $4l + 2$
(C) $2l + 1$
(D) $4l - 2$

8. The wave function for 1*s* orbital of hydrogen atom is given by:

$$\psi_{1s} = \frac{\pi}{\sqrt{2}}e^{-r/2a_0}$$

where a_0 = radius of first Bohr orbit, r = distance from the nucleus (probability of finding the electron varies with respect to it). What will be the ratio of probabilities of finding the electrons at nucleus of first Bohr's orbit a_0?
(A) e
(B) e^2
(C) $1/e^2$
(D) zero

9. For which of the species, Bohr's theory is not applicable?
(A) Be^{3+}
(B) Li^{2+}
(C) He^{2+}
(D) H

10. The number of nodal planes in d_{xy} orbital is
(A) 0
(B) 1
(C) 2
(D) 3

11. The radial wave equation for hydrogen atom is:

$$\psi = \frac{1}{16\sqrt{4}}\left(\frac{1}{a_0}\right)^{3/2}[(x-1)(x^2-8x+12)]e^{-r/2}$$

where $x = 2r/a_0$; a_0 = radius of first Bohr orbit. The minimum and maximum position of radial nodes from nucleus are:
(A) $a_0, 3a_0$
(B) $\frac{a_0}{2}, 3a_0$
(C) $\frac{a_0}{2}, a_0$
(D) $\frac{a_0}{2}, 2a_0$

12. For an electron, the product $v \times n$ (velocity × principal quantum number) will be independent of the
(A) principal quantum number.
(B) velocity of the electron.
(C) energy of the electron.
(D) frequency of its revolution.

13. When the electron of a hydrogen atom jumps from the $n = 4$ to the $n = 1$ state, the number of spectral lines emitted is
(A) 15
(B) 6
(C) 3
(D) 4

14. Assume that the potential energy of a hydrogen atom in its ground state is zero. Then its energy in the first excited state will be
(A) 13.6 eV
(B) 27.2 eV
(C) 23.8 eV
(D) 10.2 eV

15. In an atom two electrons move around the nucleus in circular orbits of radii *r* and 4*r*. The ratio of the time taken by them to complete one revolution is:
(A) 1:4
(B) 4:1
(C) 1:8
(D) 8:7

16. Which of the following postulates does not belong to Bohr's model of the atom?
(A) Angular momentum is an in the orbit is a multiple of $h/2\pi$.
(B) The electron stationed in the orbit is stable.
(C) The path of an electron is circular.
(D) The change in the energy levels of electron is continuous.

17. When the frequency of light incident on a metallic plate is doubled, the K.E. of the emitted photoelectron will be
(A) doubled.
(B) halved.
(C) increased but more than doubled of the previous K.E.
(D) remains unchanged.

18. The orbital angular momentum of an electron in 2*s* orbital is
(A) $h/4\pi$
(B) zero
(C) $h/2\pi$
(D) $\sqrt{2}h/2\pi$

19. The triad of nuclei that is isotonic is
(A) ${}^{14}_{6}C$, ${}^{15}_{7}N$, ${}^{17}_{9}F$
(B) ${}^{12}_{6}C$, ${}^{14}_{7}N$, ${}^{19}_{9}F$
(C) ${}^{14}_{6}C$, ${}^{14}_{7}N$, ${}^{17}_{9}F$
(D) ${}^{14}_{6}C$, ${}^{14}_{7}N$, ${}^{19}_{9}F$

20. The increasing order (lowest first) for the values of *e*/*m* (charge/mass) for electron (*e*), proton (*p*), neutron (*n*) and alpha particle (α) is
(A) e, p, n, α
(B) n, p, e, α
(C) n, p, α, e
(D) n, α, p, e

21. The maximum number of electrons that maybe present in all atomic orbitals with principle quantum number 3 and azimuthal quantum number 2 is
(A) 10
(B) 8
(C) 12
(D) 4

22. Rutherford's experiment on scattering of α particles showed for the first time that the atom has
(A) electrons.
(B) protons.
(C) nucleus.
(D) neutrons.

23. The radius of which of the following orbit is same as that of the first Bohr's orbit of hydrogen atom

(A) He^+ $(n = 2)$
(B) Li^{2+} $(n = 2)$
(C) Li^{2+} $(n = 3)$
(D) Be^{3+} $(n = 2)$

24. The radial distribution curve of the *d* orbital with double dumbbell shape in the fourth principle shell consists of __________ nodes.

(A) 2
(B) 0
(C) 1
(D) 3

25. The wavelength associated with a golf ball weighing 200 g and moving at a speed of 5 m/h is of the order

(A) 10^{-10} m
(B) 10^{-20} m
(C) 10^{-30} m
(D) 10^{-40} m.

26. Magnetic moments of V $(Z = 23)$, Cr $(Z = 24)$, Mn $(Z = 25)$ are x, y, z. Hence,

(A) $x = y = z$
(B) $x < y < z$
(C) $x < z < y$
(D) $z < y < x$

27. The outermost electronic configuration of the most electronegative element is

(A) ns^2np^3
(B) ns^2np^4
(C) ns^2np^5
(D) ns^2np^6

28. If $n = 6$, the correct sequence of filling of electrons will be

(A) $ns \rightarrow np \rightarrow (n-1)d \rightarrow (n-2)f$
(B) $ns \rightarrow n(n-2)f \rightarrow (n-1)d \rightarrow np$
(C) $ns \rightarrow n(n-1)d \rightarrow (n-2)f \rightarrow np$
(D) $ns \rightarrow (n-2)f \rightarrow np \rightarrow (n-1)d$

29. The first emission line in the atomic spectrum of hydrogen in the Balmer Series appears at

(A) $\frac{9R_H}{400}$ cm^{-1}
(B) $\frac{7R_H}{144}$ cm^{-1}
(C) $\frac{3R_H}{4}$ cm^{-1}
(D) $\frac{5R_H}{36}$ cm^{-1}

30. The ratio of energy of the electron in ground state of hydrogen to the electron in first excited state of Be^{3+} is

(A) 4:1
(B) 1:4
(C) 1:8
(D) 8:1

31. Correct set of four quantum numbers for the valence (outermost) electron of rubidium $(Z = 37)$ is:

(A) 5, 0, 0, +1/2
(B) 5, 1, 0, +1/2
(C) 5, 1, 1, +1/2
(D) 6, 0, 0, +1/2

32. The second line of Lyman series of H coincides with the sixth fine of Paschen series of an ionic species X. Find X assuming Rydberg constant *R* to be the same for both H and X?

(A) He^+
(B) Li^{2+}
(C) Li^+
(D) H

33. The work function for a metal is 4 eV. To emit a photoelectron of zero velocity from the surface of the metal, the wavelength of incident light should be

(A) 2700 Å
(B) 1700 Å
(C) 5900 Å
(D) 3100 Å

34. An electron in a hydrogen-like atom is in an excited state. It has a total energy of –3.4 eV, calculate the de Broglie's wavelength?

(A) 66.5 Å
(B) 6.66 Å
(C) 60.6 Å
(D) 6.06 Å

35. The ionization energy of a hydrogen atom in terms of Rydberg constant (R_H) is given by the expression.

(A) R_Hhc
(B) R_Hc
(C) $2R_Hhc$
(D) R_HhcN_A

36. The fourth line of the Balmer series corresponds to electron transition between energy levels

(A) 6 and 2
(B) 5 and 2
(C) 4 and 1
(D) 5 and 1

37. If λ_1 and λ_2 denote the de Broglie wavelengths of two particles with same masses, but charges in the ratio of 1:2 after they are accelerated from rest through the same potential difference, then

(A) $\lambda_1 = \lambda_2$
(B) $\lambda_1 < \lambda_2$
(C) $\lambda_1 > \lambda_2$
(D) None of these

38. A 1 kW radio transmitter operates at a frequency of 880 Hz. How many photons per second does it emit?

(A) 1.71×10^{21}
(B) 1.71×10^{30}
(C) 6.02×10^{23}
(D) 2.85×10^{28}

39. Which of the following electronic configurations have zero spin multiplicity?

(A) $\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$
(B) $\boxed{\uparrow}\boxed{\uparrow}\boxed{\downarrow}$
(C) $\boxed{\uparrow}\boxed{\downarrow}\boxed{\downarrow}$
(D) $\boxed{\downarrow}\boxed{\downarrow}\boxed{\downarrow}$

40. When the value of the azimuthal quantum number is 3, the maximum and the minimum values of the spin multiplicities are

(A) 4, 3
(B) 8, 1
(C) 1, 3
(D) 8, 2

41. The ratio of the radii of the first three Bohr orbits is

(A) 1:0.5:0.33
(B) 1:2:3
(C) 1:4:9
(D) 1:8:27

42. An electron has wavelength 1 Å. The potential by which the electron is accelerated will be

(A) 0.0926 V
(B) 0.0502 V
(C) 150.7 V
(D) 51.2 V

43. If 10^{-17} J of light energy is needed by the interior of human eye to see an object. The photons of green light $(\lambda = 550$ nm) needed to see the object are

(A) 27
(B) 28
(C) 29
(D) 30

44. Which of the following arrangement of two electrons in two degenerated orbitals is not possible at all?

(A) $\boxed{\uparrow}\boxed{\downarrow}$
(B) $\boxed{\uparrow\uparrow}\boxed{}$
(C) $\boxed{\uparrow\downarrow}\boxed{}$
(D) All of these

45. The number of unpaired electrons in Mn^{4+} $(Z = 25)$ is

(A) 4
(B) 2
(C) 5
(D) 3

46. Atomic number of chromium is 24, then Cr^{3+} will be

(A) diamagnetic
(B) paramagnetic
(C) ferromagnetic
(D) none of these

47. The energy for an electron is an orbit of hydrogen atom is given by $E_n = -(13.6/n^2)Z^2$ eV. Calculate the energy of the orbit having a radius $9r_1$ where r_1 is the radius of first orbit?

(A) –1.51 eV
(B) 10.2 eV
(C) 13.6 eV
(D) 1.36 eV

48. The total energy of the electron in the hydrogen atom in the ground state is –13.6 eV. The K.E. of this electron is
(A) 13.6 eV
(B) Zero
(C) –13.6 eV
(D) 6.8 eV

49. A compound of vanadium possesses a magnetic moment of 1.73 BM. The oxidation state of vanadium in this compound is
(A) 1
(B) 2
(C) 4
(D) cannot be predicted.

50. The number of spherical nodes in 3*p* orbital is
(A) 1
(B) 3
(C) 2
(D) 0

51. In a sample of hydrogen atoms, electrons make transitions from $n = 5$ to $n = 1$. If all the spectral lines are observed, then the line having the third highest energy will correspond to
(A) $5 \rightarrow 3$
(B) $4 \rightarrow 1$
(C) $3 \rightarrow 1$
(D) $5 \rightarrow 4$

52. An energy of 24.6 eV is required to remove one of the electrons from helium atom. The energy required to remove both the electrons from helium atom is
(A) 38.2 eV
(B) 49.2 eV
(C) 51.8 eV
(D) 79.0 eV

53. In ψ_{321} the sum of angular momentum, spherical nodes and angular node is
(A) $\dfrac{\sqrt{6}h + 4\pi}{2\pi}$
(B) $\dfrac{\sqrt{6}h}{2\pi} + 3$
(C) $\dfrac{\sqrt{6}h + 2\pi}{2\pi}$
(D) $\dfrac{\sqrt{6}h + 8\pi}{2\pi}$

54. The kinetic energy, *E*, of an electron is related to the kelvin temperature through the equation, $E = \frac{3}{2}kT$ where $k = 1.38 \times 10^{-23}$ J particle^{-1} K^{-1}. You are given an electron with a de Broglie wavelength of $\lambda = 76.3$ nm. What is the kelvin temperature of electron?
(A) 0.50
(B) 1.00
(C) 1.50
(D) 2.00

Multiple Correct Choice Type

1. Which of the following statements is correct about angular nodes?
(A) These nodes are directional in nature.
(B) These nodes are dependent on angle θ and ϕ.
(C) These nodes are independent from the radial wave function (R).
(D) These nodes are dependent on the radial wave function.

2. Five valence electrons of $^{30}_{15}$P are labeled as

3*s*	3*p*		
pq	*x*	*y*	*z*

If the spin quantum number of *q* and *z* is +(1/2), then the group of electrons with three of the quantum number same are
(A) *pq*
(B) (*xyz*), (*pq*)
(C) (*pq*), (*xyz*), (*pz*)
(D) (*pq*), (*xyz*), (*qy*)

3. Which of the following orbitals are associated with the angular nodes?
(A) *s* orbitals
(B) *p* orbitals
(C) *d* orbitals
(D) *f* orbitals

4. Let A_n be the area electrons by the *n*th orbit in a hydrogen atom. The graph of ln (A_n/A_1) against ln (n)
(A) will pass through origin.
(B) will be straight line with slope = 4.
(C) will be a monotonically increasing non linear curve
(D) will be a circle.

5. Choose the correct statements among the following:
(A) A node is a point in space where the wave function ψ has zero amplitude.
(B) The number of maximas (peaks) in radial distribution is $n - 1$.
(C) Radial probability density is $4\pi r^2 R^2_{nf(r)}$.
(D) $|\psi^2|$ represents probability of finding electron.

6. The quantum numbers which are derived from the solution of Schrodinger's wave equation are
(A) principal quantum number.
(B) azimuthal quantum number.
(C) magnetic quantum number.
(D) spin quantum number.

7. Which of the following is the nodal plane of d_{xy} orbital?
(A) *xy*
(B) *yz*
(C) *zx*
(D) All of these.

8. Many elements have non-integral atomic masses because
(A) they have isotopes.
(B) their isotopes have non-integral masses.
(C) their isotopes have different masses.
(D) the constituents, neutrons, protons and electrons combine to give fractional masses.

Assertion–Reasoning Type

Choose the correct option from the following:
(A) Statement 1 is True, Statement 2 is True; Statement 2 is a correct explanation for Statement 1.
(B) Statement 1 is True, Statement 2 is True; Statement 2 is not a correct explanation of Statement 1.
(C) Statement 1 is True; Statement 2 is False.
(D) Statement 1 is False, Statement 2 is True.

1. **Statement 1:** Hydrogen has one electron in its orbit but it produces several spectral lines.

Statement 2: There are many excited energy levels available.

2. **Statement 1:** Maximum possible number of electrons in any energy level is fixed.

   Statement 2: Total number of electrons in a shell = 2 $(2l + 1)$.

3. **Statement 1:** The number of radial nodes for $3p$ orbital is 1.

   Statement 2: Number of radial nodes = l.

4. **Statement 1:** Photoelectric effect is easily pronounced by caesium metal.

   Statement 2: Photoelectric effect is easily pronounced by the metals having high ionization enthalpy.

5. **Statement 1:** Electronic energy for hydrogen atom of different orbitals follow the following sequence: $1s < 2s = 2p < 3s = 3p = 3d$.

   Statement 2: Electronic energy for hydrogen atom depends only on n and is independent of l and m_l values.

Comprehension Type

Read the paragraphs and answer the questions that follow.

Paragraph I

The wave functions for any one-electron system, such as hydrogen atom, can be expressed as $\psi = k^r\ e^{-\kappa r}$ where k and k^r are constants. For hydrogen atom, we have

$$\psi_{1s} = \sqrt{\frac{1}{\pi a_0^3}} \cdot e^{\frac{Zr}{a_0}}$$

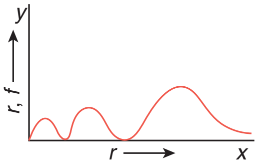
$$\psi_{2s} = \left(\frac{Z}{2a_0}\right)^{1/2}\left(2 - \frac{Zr}{a_0}\right)e^{\frac{Zr}{a_0}}$$

The number of angular nodes is given by the value of angular quantum number and angular node is directional in nature. The total number of nodes is nothing but the sum of radial nodes $(n - l - 1)$ and angular nodes (l).

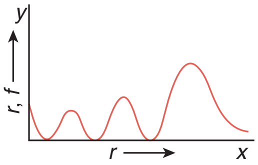
1. If the nodes at infinity are not neglected, then what is the total number of radial and angular nodes of $3p_x$ orbitals?
   (A) 4 (B) 3
   (C) 5 (D) infinity

2. Which of the following is the correct representation of plot radial function (r, f) in y-axis vs. distance from the nucleus in x-axis for 1-electron of $3p$ atomic orbital?

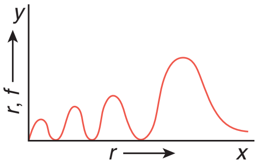
(A)



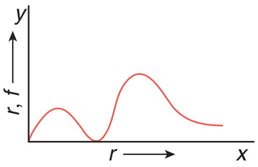
(B)



(C)



(D)



3. The distance from the nucleus of the radial node of $2s$ electron of Li^{2+} ion (a_0 = Bohr's radius) is equal to
   (A) $0.67a_0$ (B) $2a_0$
   (C) a_0 (D) $0.5a_0$

Paragraph II

Heisenberg gave the principle that there is uncertainty in simultaneous measurement of position and momentum of small particles. If any one of these two quantities is measured with higher accuracy, the measurement of the other becomes less accurate. The product of the uncertainty in position (Δx) and uncertainty in momentum (Δp) is always constant and is equal to or greater than $h/4\pi$, where h is Planck's constant.

4. The uncertainty in position of an electron ($m = 9.1 \times 10^{-28}$ g) moving with a velocity 3×10^4 cm s^{-1} accurate upto 0.001% will be
   (A) 3.84 cm (B) 1.92 cm
   (C) 7.68 cm (D) 5.76 cm

5. Uncertainty in position is twice the uncertainty in momentum, uncertainty velocity is
   (A) $\sqrt{\frac{h}{\pi}}$ (B) $\frac{1}{2m}\sqrt{\frac{h}{\pi}}$
   (C) $\frac{1}{2m}\sqrt{h}$ (D) $\frac{1}{2\sqrt{2}m}\sqrt{\frac{h}{\pi}}$

6. If uncertainty in the position of an electron is zero, the uncertainty in its momentum would be
   (A) zero (B) $<h/4\pi$
   (C) $>h/4\pi$ (D) infinite

Paragraph III

For one-electron species, the wave number of radiation emitted during the transition of electron from a higher energy state (n_2) to a lower energy state (n_1) is given by:

$$\bar{\nu} = \frac{1}{\lambda} R_H \times Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad (1)$$

where $R_H = \frac{2\pi m_e k^2 e^4}{h^3 c}$ is Rydberg constant for hydrogen atom.

Now, considering nuclear motion, the most accurate measurement would be obtained by replacing mass of electron (m_e) by the reduced mass (μ) in the above expression, defined as

$$\mu = \frac{m_n \times m_e}{m_n + m_e}$$

where m_n = mass of nucleus. For Lyman series, $n_1 = 1$ (fixed for all the lines) while n_2 = 2, 3, 4…. For Balmer series: $n_1 = 2$ (fixed for all the lines) while $n_2 = 3, 4, 5$…..

7. If proton in hydrogen nucleus is replaced by a positron having the same mass as that of proton but same charge as that of proton, then considering the nuclear motion, the wavenumber of the lowest energy transition of He^+ ion in Lyman series will be equal to

(A) $2R_H$ (B) $3R_H$
(C) $4R_H$ (D) R_H

8. The ratio of the wave numbers for the highest energy transition of electron in Lyman and Balmer series of hydrogen atom is

(A) 4:1 (B) 6:1
(C) 9:1 (D) 3:1

Integer Answer Type

The answer is a **non-negative integer.**

1. The wave function of an orbital is represented as ψ_{420}. The azimuthal quantum number of the orbital is __________.

2. The number of spectral lines produced when an electron jumps from 5th orbit to 2nd orbit in the hydrogen atom is __________.

3. The Schrödinger wave equation for hydrogen atom is

$$\psi_{2s} = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{\frac{3}{2}}\left(x^2 - \frac{r}{a_0}\right)^{e^{-1/a_0}}$$

where a_0 is Bohr's radius. If the radial node in 2s be at $r = 4a_0$ then x would be equal to __________.

4. The angular momentum of an electron is h/π. The Bohr's orbit in which the electron is revolving is __________.

5. Magnetic moment of M^{x+} is $\sqrt{24}$ BM. The number of unpaired electrons in M^{x+} is __________.

6. The number of nodes in the radial distribution curve of 2s orbital is __________.

7. The number of electrons with $l = 2$ in the ground state of chromium atom is __________.

8. The circumference of the second orbit of electron in hydrogen atom is 400 nm, the de Broglie wavelength of electron corresponding to the circumference of same orbit is 200 nm. The number of waves made by an electron is __________.

9. The value of n of the highest excited state that an electron of hydrogen atom in the ground state can reach when 12.09 eV energy is given to the hydrogen atom is __________.

10. The number of d electrons in Cu^{2+} (atomic number = 29) that can have the spin quantum (–1/2) is __________.

11. The number of elements that have the last electron with quantum numbers of $n = 4$ and $l = 1$ is __________.

Matrix–Match Type

1. Match the atoms/ions with the characteristics of the electron they contain.

Column-I	Column-II
(A) H	(p) Radius of 4th orbital = 0.53 × 4 Å
(B) He^+	(q) Energy of 2nd orbit = –13.6 eV
(C) Be^{2+}	(r) Radius of 2nd orbit = 0.53 × 4 Å
(D) Li^{3+}	(s) Velocity of electron in the 3rd orbit = 2.18×10^8 Å
	(t) Energy of 4th orbit = –13.6 eV

2. Match the angle between the axes of the orbitals with their value.

Column I	Column II
(A) The angle between the z-component of orbital angular momentum of electron of p_x atomic orbital and z- axis (assume $m = +1$)	(p) 135°
(B) The angle between the z-component of orbital angular momentum of electron of p_z of atomic orbital and z-axis.	(q) 45°
(C) The angle between the z-component of orbital angular momentum of electron of p_y atomic orbit and z-axis is	(r) Less than 45° or more than 135°
(D) The angle between the z-component of orbital angular momentum of electron of $3d_{x^2-y^2}$ orbital and z-axis.	(s) 90°

3. Match the series of hydrogen spectrum with their characteristics.

Column I	Column II
(A) Lyman series	(p) Visible region
(B) Balmer series	(q) Infrared region
(C) Paschen series	(r) Ultraviolet region
(D) Bracket series	(s) $n_2 = 4$ to $n_2 = 3$
	(t) $n_2 = 5$ to $n_2 = 1$

4. Match the orbitals with the number of nodes/quantum numbers present in them.

Column I	Column II
(A) 2*p* orbital	(p) Number of spherical nodes = 0
(B) 3*d* orbital	(q) Number of nodal plane = 0
(C) 2*s* orbital	(r) Orbital angular momentum number = 0
(D) 4*f* orbital	(s) Azimuthal quantum number = 0

5. Match the name of the equation with its expression.

Column I	Column II
(A) Moseley's equation	(p) $\sqrt{l(l+1)}\,\dfrac{h}{2\pi}$
(B) Potential energy of electron	(q) $\dfrac{eh}{2\pi mc}\sqrt{m_s(m_s+1)}$
(C) Orbital angular momentum	(r) $\dfrac{Zke^2}{r_n}$
(D) Spin magnetic moment	(s) $\sqrt{\nu} = a(Z-b)$

ANSWERS

Review Questions

1. **(a)** Radium-226: neutrons = 138; protons = 88; electrons = 88

(b) ^{206}Pb: neutrons = 124; protons = 82; electrons = 82

(c) Carbon-14: neutrons = 8; protons = 6; electrons = 6

(d) ^{23}Na: neutrons = 12; protons = 11; electrons = 11

2. Amplitude; wavelength; frequency or wavelength

5. Nucleus

6. Gamma rays < X rays < ultraviolet < visible < infrared < microwaves < TV waves

7. Wave mechanics and quantum mechanics

9. **(a)** Yellow; **(a)** 5.09×10^{14} s^{-1}; **(c)** 3.37×10^{-19} J

10. Symbol *a* corresponds to the mass number while symbol *b* corresponds to the atomic number.

11. Part **(c)** is correct.

12. ^{22}Ne = 10%

13. $n = 4$, $l = 3, 2, 1, 0$; $m_l = -3$ to $+3$ and $m_s = +1/2$.

17. **(a)** Lyman – Ultraviolet; Balmer – Visible; Paschen, Brackett, Pfund – Infrared; **(b)** $\bar{\nu} = R\left(\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right)$

18. **(a)** 6*d*, **(b)** 4*f*, **(c)** 4*d* and **(d)** 5*g*

19. The size of orbital increases with increase of the principal quantum number *n*.

21. $n_2 = 5$

23. $\Delta x = 5.27 \times 10^{-24}$ m

24. Frequency = 0.0058×10^{17} s^{-1}; Energy = 0.038×10^{-17} J

25. 0.65×10^{15} s^{1}

26. Principal quantum number ($n = 1, 2, 3, 4$); azimuthal quantum number ($l = 0$ to $n - 1$); magnetic quantum number ($m_l = 2l + 1$); spin quantum number ($m_s = +1/2$ or $-1/2$)

28. H, He^{+}, Li^{2+}, Be^{3+}.

30. $\Delta p \geq 0.527$

Numerical Problems

1. ^{20}F

2. $^{27}_{13}$Al^{3+}

3. 3×10^{10} to 3×10^{12} Hz
4. 0.773 m
5. 17.015 cm
6. 3.58×10^{-19} J
7. 1.07×10^{-19} J
8. Wavelength = 1.28×10^{-6} cm; frequency = 2.34×10^{14} Hz
9. Excited state; Yes
10. 0.4761 nm
11. 0.2645 nm
12. 6.97×10^{-19} J
13. 2.607 10^{-10} m
14. **(a)** -8.72×10^{-20} J; **(b)** 1.3225 nm
15. 367 nm
16. 4525.6
17. Violet light: frequency = 6.6×10^{14} Hz, wave number = 2.2×10^{12} m^{-1}; red light: frequency = 4×10^{14} Hz, wave number = 1.33×10^{-12} m^{-1}.
18. 5.9842 times
19. 2.165×10^{-20} J $atom^{-1}$
20. **(a)** 4.97×10^{-19} J; **(b)** 8.58×10^{-28} J
21. Frequency = 6.17×10^{14} Hz; wavelength = 486 nm
22. -145.7 kJ mol^{-1}; $n = 3$
23. Frequency = 2.34×10^{14} Hz s; wavelength = 1.286×10^{-6} m
24. The wavelengths of light from the two transitions are very close together.
25. 5.76×10^{-6} m s^{-1}
26. 4.15

Additional Objective Questions

Single Correct Choice Type

1. (B)
2. (D)
3. (B)
4. (B)
5. (B)
6. (A)
7. (A)
8. (D)
9. (C)
10. (C)
11. (B)
12. (A)
13. (B)
14. (C)
15. (C)
16. (D)
17. (C)
18. (B)
19. (A)
20. (D)
21. (A)
22. (C)
23. (D)
24. (C)
25. (C)
26. (C)
27. (C)
28. (B)
29. (D)
30. (B)
31. (A)
32. (B)
33. (D)
34. (B)
35. (A)
36. (A)
37. (C)
38. (B)
39. (C)
40. (D)
41. (C)
42. (C)
43. (B)
44. (B)
45. (D)
46. (B)
47. (A)
48. (A)
49. (C)
50. (A)
51. (C)
52. (D)
53. (A)
54. (D)

Multiple Correct Choice Type

1. (A, B, C)
2. (A, B)
3. (B, C, D)
4. (A, B, C)
5. (A, B, C, D)
6. (A, B, C)
7. (B, C)
8. (A, C)

Assertion–Reasoning Type

1. (A)
2. (C)
3. (C)
4. (C)
5. (A)

Comprehension Type

1. (B)
2. (D)
3. (A)
4. (B)
5. (D)
6. (D)
7. (B)
8. (A)

Integer Answer Type

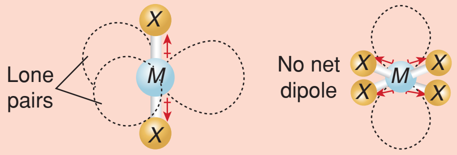
1. (2)
2. (6)
3. (2)
4. (2)
5. (4)
6. (1)
7. (5)
8. (2)
9. (3)
10. (5)
11. (6)

Matrix–Match Type

1. A → (r); B → (q), C → (p, t), D → (s)
2. A → (q); B → (s), C → (p), D → (r)
3. A → (r, t); B → (p), C → (q, s), D → (q)
4. A → (p); B → (p), C → (q, r, s), D → (p)
5. A → (s); B → (r), C → (p), D → (q)

6

Chemical Bonding



Exceptions having no dipole moment

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6.4 Covalent Bonding
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6.6 Valence Bond Theory
6.7 Hybridization
6.8 The Valence Shell Electron Pair Repulsion (VSEPR) Theory and Shapes of Simple Molecules
6.9 Back Bonding
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6.11 Dipole Moment
6.12 Resonance Structures
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A bond is a *force* existing between atoms in a molecule that holds the atoms together. It is the same kind of electrostatic attraction that binds the electrons of an atom to its positively charged nucleus. The existence of a stable polyatomic species, whether element or compound, implies that atoms can act upon each other to form aggregates having lower energy than separated fragments. When this energy lowering exceeds approximately 10 kcal mol^{-1} of atoms, then a chemical bond is said to be formed.

There is no single satisfactory theory which would explain the concept of bonding in all types of compounds and also predict their structures, energies and properties. Initially, the concept of a chemical bond was explained by a few classical models which assume that electrons and ions behave as point charges that attract and repel according to the laws of classical mechanics and electrostatics. However, these models apply only to certain classes of compounds and explain only a restricted range of phenomena. Since the development of quantum theory in 1920s, the chemical bond has been explained by quantum mechanical models. We shall look into the different models proposed and different kinds of bonds in this chapter.

6.1 | CHEMICAL BOND FORMATION – KÖSSEL–LEWIS APPROACH

In 1916, Kössel and Lewis made the first breakthrough explaining the formation of chemical bond by proposing a theory known as the **electronic theory of valency**. The theory was based on the following observations:

1. The electrons in the outermost shell/orbit of an atom are called valence shell electrons. These are responsible for most of the properties of the elements.

2. Elements which have two or eight electrons in the outermost shell, that is, have their octet complete are stable and do not combine chemically either with each other or other elements.

According to the theory, the formation of a chemical bond between two or more atoms can be explained as tendency of elements to attain stable configuration of electrons in the outermost shell (Table 6.1). The combination of atoms led to rearrangement of their electrons either by complete transfer of electrons from one atom to another or by sharing of electrons.

Table 6.1 Electronic structures

Element	Symbol	Electronic structure
Helium	He	$1s^2$
Neon	Ne	$[\mathrm{He}]\ 2s^2\ 2p^6$
Argon	Ar	$[\mathrm{Ne}]\ 3s^2\ 3p^6$
Krypton	Kr	$[\mathrm{Ar}]\ 3d^{10}\ 4s^2\ 4p^6$
Xenon	Xe	$[\mathrm{Kr}]\ 4d^{10}\ 5s^2\ 5p^6$
Radon	Rn	$[\mathrm{Xe}]\ 4f^{14}\ 5d^{10}\ 6s^2\ 6p^6$

Concept of Electrovalent Bond (or Ionic Bond)

An ionic bond is formed when an element having a high tendency to loose electrons (an electropositive element) combines with an element which has a high tendency to accept electrons (an electronegative element). For example, ionic compounds are formed when metals react with non-metals. NaCl is formed from its elements, with each sodium atom losing one electron to form a sodium ion, $\mathrm{Na^+}$, and each chlorine atom gains one electron to become a chloride ion, $\mathrm{Cl^-}$.

$$\underset{\text{Sodium atom}}{\mathrm{Na}} \rightarrow \underset{\text{Sodium ion}}{\mathrm{Na^+}} + e^-$$

$$\underset{\text{Chlorine atom}}{\mathrm{Cl}} + e^- \rightarrow \underset{\text{Chlorine ion}}{\mathrm{Cl^-}}$$

Once formed, these ions become tightly packed together because their opposite charges attract. This attraction between positive and negative ions in an ionic compound is what we call an **ionic bond**. In NaCl, electrostatic forces holding the ions in place in the solid constitute ionic bonds.

Kössel postulated the important features of formation of this type of chemical bond which formed the basis for the modern concept of **ionic bonding** in crystalline solids.

1. In the periodic table, the highly electronegative halogens and electropositive alkali metals are separated by noble gases.
2. The formation of a positive ion from an atom is associated with loss of electrons and formation of a negative ion is associated with a gain of electrons.
3. The driving force for the formation of positive and negative ions is to attain noble gas configuration, which is associated with extra stability.
4. The bond formation between negative and positive ions is stabilized by electrostatic attraction.
5. The bond that results from electrostatic attraction between the positive and negative ions was called electrovalent bond. The term electrovalence was used to represent the number of units of charge involved in the bond formation or the charge on the participating ions. For example, in sodium chloride, sodium is assigned electrovalence one.

Lewis Representation

We have seen that in formation of a chemical bond, only the valence electrons take part, whereas the inner shell electrons are protected and do not participate in bond formation. A simple notation to represent the atom with its valence electrons using dots was introduced by American chemist G.N. Lewis and this notation is known as **Lewis symbol**. It is a symbol in which the electrons in the valence shell of an atom or an ion are represented by dots place around the symbol of the atom. For example, the Lewis symbols for elements of first, second and third period are shown in Fig. 6.1.

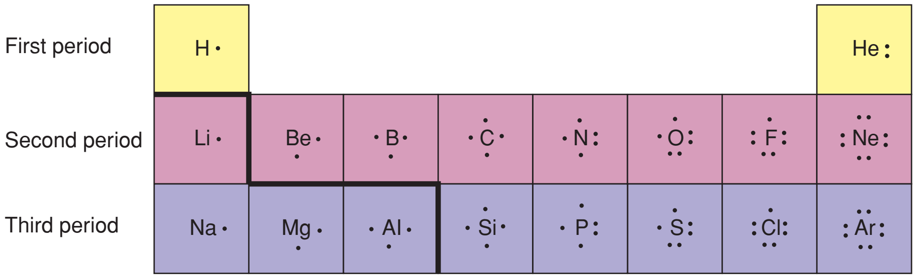
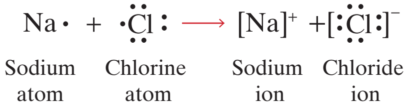
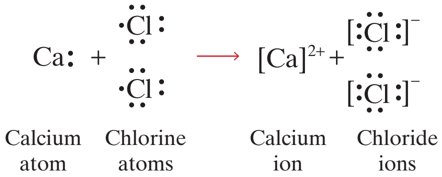


Figure 6.1 Lewis symbols for elements of first, second and third periods.

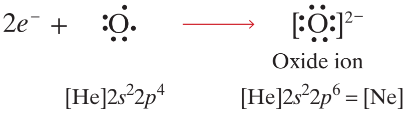
The structure of a molecule using the Lewis symbols is known as Lewis structure. The formation of sodium chloride can be expressed in terms of Lewis structure/diagram as



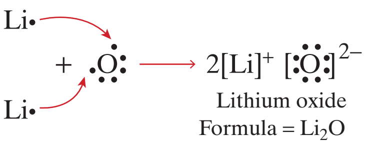
The formation of calcium chloride $CaCl_2$ may be considered in a similar way. Ca atoms have two electrons in their outer shell, so each Ca atom loses two electrons to two Cl atoms, forming a calcium ion Ca^{2+} and two chloride ions Cl^-. Showing the outer electrons only, this may be represented as follows:



Consider what happens to the electrons when lithium metal comes into contact with the oxygen in the air. An oxygen atom needs two electrons to achieve an octet and form an anion with a –2 charge. This way, oxygen attains the noble gas configuration of neon.



Since a lithium atom can lose only one electron, two lithium atoms are needed to supply the two electrons. Recall that the two +1 ions balance the charge of the one –2 ion [i.e., 2(+1) – 2 = 0]. The chemical formula of the compound lithium oxide is therefore Li_2O.



Note: The number of valence electrons helps in calculating the group valence of the elements, which is generally equal to number of dots around the symbol or 8 minus the number of dots.

Octet Rule

All the noble gases except for helium have filled outer *s* and *p* subshells (e.g., $ns^2\ np^6$). Since this is a total of eight electrons, it is referred to as an *octet* of electrons, which forms a particularly stable configuration. When the elements form ions, atoms of most of the representative elements tend to gain or lose electrons until they have obtained a configuration identical to that of the nearest noble gas. This rule has become known as the **octet rule**, which can be stated as follows: *Atoms tend to gain or lose electrons until they have achieved an outer shell that contains an octet of electrons (eight electrons)*.

Concept of Covalent Bond

A covalent bond is formed when there are two electronegative elements having a very small difference in electronegativity, for example when non-metals combine with each other to form molecules, the lowering of energy happens due to electron sharing. Another theory, the Lewis–Langmuir theory is very successful in explaining the bonding between many compounds based on the concept of shared electron pair. According to this theory, when two atoms come together, the valence electrons of each of the atoms will be attracted and shared by the nuclei of both the atoms; as a result, a net strong bonding occurs between the two atoms and is called the **covalent bond**.

Lewis Representation

For Lewis dot structures for covalent bonds, the bonds are formed by electron sharing and the atoms forming the bonds share at least one electron each to the shared pair. The atoms forming covalent bonds attain the outer shell noble gas configurations as a result of electron sharing.

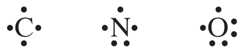
The shared pair of electrons is shown between the atoms involved in covalent bonding, while the covalent bond is shown as a horizontal line between the atoms. Such a covalent bond is known as a single bond and represents a pair of electrons shared.

For example, an isolated hydrogen atom possesses only one electron, but *two* hydrogen atoms can share their electrons so that the resulting covalent bond gives each atom an inert gas electron configuration; the formation of H_2 can be depicted as:

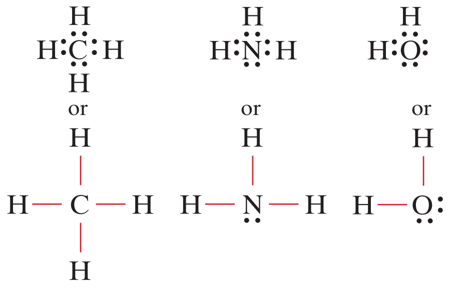
$$\mathrm{H(g) + H(g) \rightarrow H : H \text{ or } H - H(g)}$$

Before joining, each of the separate hydrogen atoms has one electron in a 1*s* orbital. When these electrons are shared, the 1*s* orbital of each atom is, in a sense, filled. Because the electrons now share the same space, they become paired. In general, the electrons involved almost always become paired when atoms form covalent bonds. In fact, a covalent bond is sometimes referred to as an **electron pair bond**. As a covalent bond does not (generally) lead to the formation of electrically charged atoms, it is also known as a homopolar bond.

There are many non-metals that form more than one covalent bond. For example, the three most important elements in biochemical systems are carbon, nitrogen and oxygen.



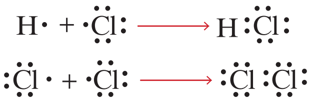
The simplest hydrogen compounds of these elements are methane CH_4, ammonia NH_3 and water H_2O. Their Lewis structures are as follows:



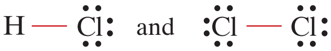
Methane Ammonia Water

Octet Rule

The octet rule can also be used to explain **the number of covalent bonds** an atom forms. This number normally equals the number of electrons the atom must acquire to have a total of eight (an octet) in its outer shell. For instance, the halogens all have seven valence electrons. The Lewis symbol for a typical member of this group, chlorine, is $\cdot\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}}\colon$. We can see that only one electron is needed to complete its octet. Of course, chlorine can actually gain this electron and become a chloride ion (as in case of sodium chloride). But when chlorine combines with another non-metal, the complete transfer of an electron is not energetically favorable. Therefore, in forming compounds such as HCl or Cl_2, chlorine gets the one electron it needs by forming a covalent bond.



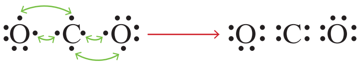
The HCl and Cl_2 molecules can also be represented using dashes for the bonds.



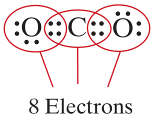
Types of Covalent Bonds

The bond produced by the sharing of *one* pair of electrons between two atoms is called a **single bond**.

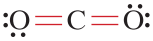
There are many molecules in which more than a single pair of electrons is shared between two atoms. For example, we can draw the formation of the bonds in CO_2 as follows.



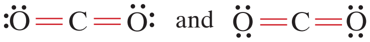
The central carbon atom shares two of its electrons with each of the oxygen atoms, and each oxygen shares two electrons with carbon. The result is the formation of two **double bonds**. Notice that in the Lewis formula, both of the shared electron pairs are placed between the symbols for the two atoms joined by the double bond. Once again, if we circle the valence shell electrons that "belong" to each atom, we see that each has an octet.



The Lewis structure for CO_2, using dashes, is

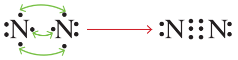


Note: The locations of the unshared pairs of electrons around the oxygen are unimportant. Two equally valid Lewis structures for CO_2 are

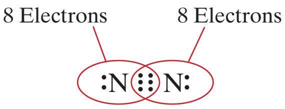


Sometimes, three pairs of electrons are shared between two atoms. The most abundant gas in the atmosphere, nitrogen, occurs in the form of diatomic molecules, N_2. The Lewis symbol for nitrogen is

and each nitrogen atom needs three electrons to complete its octet. When the N_2 molecule is formed, each of the nitrogen atoms shares three electrons with the other.



The result is called a **triple bond**. Again, notice that we place all three electron pairs of the bond between the two atoms. We count all of these electrons as though they belong to both of the atoms. Each nitrogen, therefore, has an octet.



The triple bond is usually represented by three dashes, so the bonding in the N_2 molecule is normally shown as

$$:\mathrm{N}\equiv\mathrm{N}:$$

Exceptions to the Octet Rule

The octet rule which states that bonds are formed by atoms in order to achieve the eight electrons configuration in the valence shell applies quite well to the elements of the second row of the periodic table. This is because, for the second period elements, the only available orbitals are s^2p^6 which when filled comprises the octet. Beyond the second row, it is generally applicable only to the non-transition elements. It does not work so well for the transition metals and post-transition metals (the metals that follow a row of transition metals) (Fig. 6.2).

The octet rule, as applied to ionic compounds, really works well only for the cations of the Group 1 and 2 metals and for the anions of the non-metals. It works well to explain the structure of most of the organic compounds.

However, there are exceptions to the octet rule and these are discussed as follows.

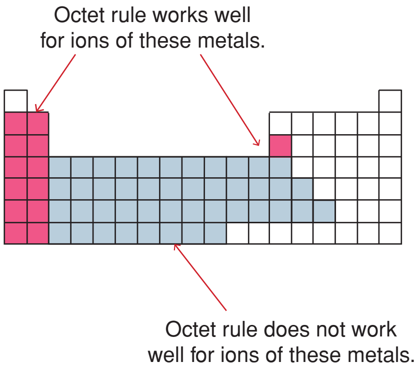
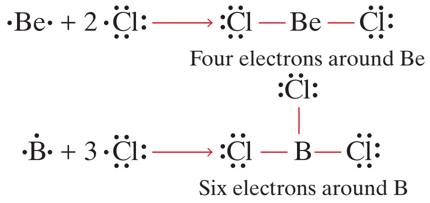

Octet rule works well for ions of these metals.
Octet rule does not work well for ions of these metals.

Figure 6.2 Exceptions to octet rule.

The Incomplete Octet of the Central Atom

There are also some molecules (but not many) in which the central atom behaves as though it has less than an octet. The most common examples involve compounds of beryllium and boron.



Although Be and B sometimes have less than an octet, the elements in Period 2 never *exceed* an octet. The reason is because their valence shells, having $n = 2$, can hold a maximum of only 8 electrons. (This explains why the octet rule works so well for atoms of carbon, nitrogen and oxygen.)

Odd-Electron Molecules

Some molecules have an odd number of valence electrons, such as nitric oxide (NO – 11 valence electrons) and nitrogen dioxide (NO_2 – 17 valence electrons). In both of these cases the nitrogen has access to fewer than 8 electrons.

$$:\dot{\mathrm{N}}=\ddot{\mathrm{O}}:$$

Note that it is a correct Lewis representation that *does not* follow octet rule.

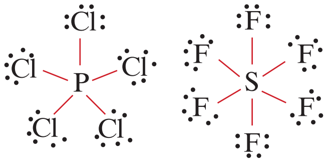
Note: When there are an odd number of electrons in a molecule it is known as a **free radical**. Due to the lack of the stability associated with a filled octet and paired electrons, free radicals are highly reactive species.

The Expanded Octet

Elements in rows below second row, such as phosphorus and sulphur, sometimes do exceed an octet, because their valence shells can hold more than 8 electrons. For example, the valence shell for elements in third row, for which $n = 3$, can hold a maximum of 18 electrons, and the valence shell for fourth row elements, which have s, p, d and f subshells, can hold as many as 32 electrons.

For elements in the third period (Na through Cl) and beyond, the higher empty orbitals ($3d$), being closer in energy to $3p$ level, can be used to accommodate additional shared pairs beyond the octet. Hence, the elements such as S, Cl, P and Si form compounds in which five or six electron pairs surround the central atom. These pairs may all be shared with other atoms, or some of them may remain as lone pairs. For example, PF_3 obeys the octet rule, but PF_5 does not. PF_5 has 10 outer electrons, and uses one 3*s*, three 3*p* and one 3*d* orbitals.

Examples of molecules in which the central atom contains an expanded octet are phosphorus pentahalide and sulphur hexafluoride, whose Lewis structures are



In these molecules, the formation of more than four bonds to the central atom requires that the central atom have a share of more than eight electrons. With the exception of second row elements like carbon and nitrogen, most non-metals can have more than an octet of electrons in the outer shell.

Other Exceptions to the Octet Theory

1. The octet rule does not work in molecules which have an odd number of electrons, such as NO and ClO_2, nor does it explain why O_2 is paramagnetic and has two unpaired electrons.

Note: The Lewis structure of oxygen can be represented as

$$:\ddot{O}=\ddot{O}:$$

The structure has only paired electrons and is expected to be diamagnetic (i.e., the compound is weakly repelled by a magnetic field). But molecular oxygen is known to be paramagnetic (i.e., molecular oxygen is weakly attracted by a magnetic field) and paramagnetic substances have at least one unpaired electron in their molecules. Therefore, the octet theory and writing Lewis structure fail in the case of molecular oxygen.

2. The octet rule was postulated on the basis of inert behavior and lack of reactivity of noble gases. However, some compounds of noble gases, such as those of xenon and krypton with oxygen and fluorine (xenon with fluorine) are known.
3. It does not account for the shapes of molecules and the relative stability of structures.

Solved Example 6-1

What types of bonding is present in KCN?

Solution

The bonding between potassium ion and cyanide ion is ionic while that between carbon and nitrogen is covalent.

$$[K]^+ \underbrace{\qquad}_{\text{Ionic bond}} [:C \underset{\text{Covalent bond}}{\equiv} N:]^-$$

Solved Example 6-2

Why doesn't hydrogen obey the octet rule? How many covalent bonds does a hydrogen atom form?

Solution

Since the outer shell (or valence shell) of hydrogen can hold only two electrons, hydrogen is not said to obey the octet rule. It does, however, readily satisfy its requirement for a closed shell electron configuration through the formation of one covalent bond.

Solved Example 6-3

How many electrons are in the valence shells of **(a)** Be in $BeCl_2$, **(b)** B in BCl_3, and **(c)** H in H_2O?

Solution

(a) Four electrons or two bonding pairs; **(b)** six electrons, all in bonding pairs; **(c)** two electrons for each hydrogen.

Solved Example 6-4

Nitrogen and arsenic are in the same group in the periodic table. Arsenic forms both $AsCl_3$ and $AsCl_5$, but with chlorine, nitrogen only forms NCl_3. On the basis of the electronic structures of N and As, explain why this is so.

Solution

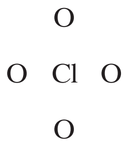
N is in the second period, it can only have an octet of electrons, so it cannot form five bonds. Whereas, As is in the fourth row, so it can have an expanded octet and form five bonds; therefore, it can form $AsCl_3$ and $AsCl_5$.

6.2 | LEWIS STRUCTURES OF SIMPLE MOLECULES

Lewis structures are very useful in chemistry because they give us a relatively simple way to describe the structures of molecules. Lewis structure can also be used to make reasonably accurate predictions about the shape of a molecule. They can be written by following a set of systematic steps that are also outlined as follows:

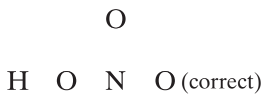
1. **Decide which atoms are bonded to each other:** Many times, the formula suggests the way the atoms are arranged because the central atom, which is usually the least electronegative one, is usually written first. Examples are CO_2 and ClO_4^-, which have the following *skeletal structures* (i.e., arrangements of atoms):

$$O \quad C \quad O$$



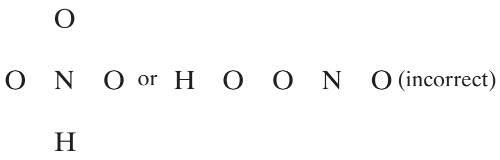
$$\begin{array}{ccc} & O & \\ O & Cl & O \\ & O & \end{array}$$

Sometimes, obtaining the skeletal structure is not quite so simple, especially when more than two elements are present. However, some generalizations are possible. For example, the skeletal structure of nitric acid, HNO_3, is



$$\begin{array}{cccc} & & O & \\ H & O & N & O \end{array} \text{ (correct)}$$

rather than one of the following:



$$\begin{array}{ccc} & O & \\ O & N & O \\ & H & \end{array} \text{ or } H \quad O \quad O \quad N \quad O \text{ (incorrect)}$$

This is because nitric acid is an oxoacid, and the hydrogen atoms that can be released from molecules of oxoacids are always bonded to oxygen atoms, which are in turn bonded to the third non-metal atom. Therefore, recognizing HNO_3 as the formula of an oxoacid allows us to predict that the three oxygen atoms are bonded to the nitrogen, and the hydrogen is bonded to one of the oxygens.

Note: There are times when no reasonable basis can be found for choosing a particular skeletal structure. If you must make a guess, choose the most symmetrical arrangement of atoms, because it has the greatest chance of being correct.

2. **Count all of the valence electrons:** This is done to find out how many dots must appear in the final formula. Using the periodic table, locate the groups in which the elements in the formula occur to determine the number of valence electrons contributed by each atom. If the structure you wish to draw is that of an ion, *add one additional valence electron for each negative charge or remove a valence electron for each positive charge*. Some examples are

NH_4^+	Nitrogen (Group 15) contributes $5e^-$.	$1 \times 5 = 5e^-$
	Each hydrogen (Group 1) contributes $1e^-$.	$4 \times 1 = 4e^-$
	Subtract $1e^-$ for the $1+$ charge.	$-1e^-$
		Total $8e^-$

3. **Distribute the total number of electrons as bonding shared pairs:** This distribution is done between the atoms of the molecules in proportion to the number of bonds formed by them.
4. **Place double and triple bonds where necessary:** Once the shared pairs of electrons have been used up to form single bonds, the remaining electron pairs can be used to form multiple bonds (double or triple) or they continue to remain as lone pairs on the atoms. The basic requirement to be met is that the octet of each atom is complete. Lewis structure representations of some molecules are given in the Fig. 6.3.

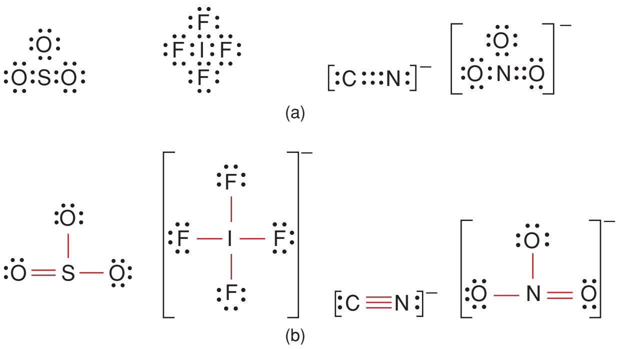


Figure 6.3 Lewis structure representations of molecules using (a) only Lewis dots; (b) Lewis dots and bonds.

Solved Example 6-5

Why can H never serve as the central atom in a Lewis structure?

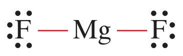
Solution

Hydrogen needs only two electrons in its outer shell in order to achieve the electron configuration of He. Therefore, hydrogen is capable of forming only one bond and cannot serve as the central atom in a Lewis structure.

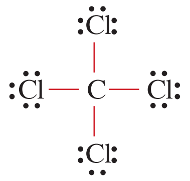
Solved Example 6-6

Draw the Lewis electron-dot diagrams for MgF_2, CCl_4, OH^- and PCl_6.

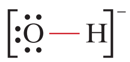
Solution



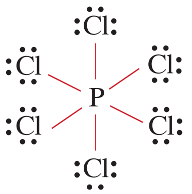
Magnesium fluoride MgF_2



Carbon tetrachloride CCl_4



Hydroxide anion OH^-



Phosphorus hexachloride PCl_6

Solved Example 6-7

How many valence electrons should appear in the Lewis structures of SO_2, SeO_4^{2-}, and NO^+?

Solution

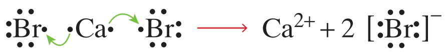
SO_2, SeO_4^{2-} and NO^+, respectively, contain 18 $(6 + 2\times6)$, 32 $(6 + 4\times6 + 2)$ and 10 $(5 + 6 - 1)$ valence electrons.

Solved Example 6-8

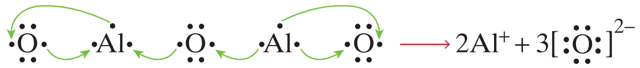
Use Lewis symbols to diagram the decomposition reactions of **(a)** $CaBr_2$, **(b)** Al_2O_3, and **(c)** KS_2

Solution

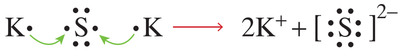
(a)



(b)



(c)



6.3 | FORMAL CHARGE

In case of polyatomic ions, the charge is represented as the net charge on the ion. However, it is possible to assign formal charge to each atom. Formal charge is the charge that each atom in a molecule would have if the electrons in the bonds were divided equally between the two atoms. It considers all bonds as if they were non-polar. In other words, it is the difference between the number of valence electrons of that atom in isolated state and the number of electrons assigned to it in the Lewis structure.

Note: Formal charge is a method of electron book-keeping and does not imply that it is the actual charge on the atom in question.

Calculating the Formal Charge on an Atom

Step 1: Write down the number of valence electrons in an isolated atom of the element.

Step 2: Using the Lewis structure, add up the valence electrons that "belong to" the atom in the molecule or ion, and then subtract this total from the value in Step 1.

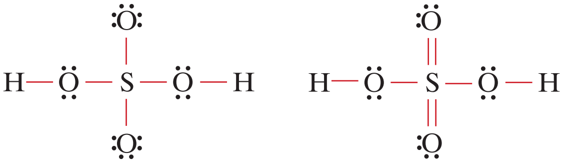
In performing the calculation in Step 2, electrons in bonds are divided equally between the two atoms, while unshared electrons are assigned exclusively to the atom on which they reside. Therefore, the calculation of formal charge is summarized by the following equation:

$$\begin{array}{c}\text{Formal}\\\text{charge}\end{array} = \left(\begin{array}{c}\text{Number of } e^- \text{ in valence}\\\text{shell of the isolated atom}\end{array}\right) - \overbrace{\left(\begin{array}{l}\text{Number of bonds}\\\text{to the atom}\end{array} + \begin{array}{l}\text{Number of}\\\text{unshared } e^-\end{array}\right)}^{\begin{array}{c}\text{Calculated number of electrons in the valence shell}\\\text{of the atom in the Lewis structure.}\end{array}}$$

The formal charge on an atom is also calculated by noting the number of valence electrons (V_a) on a neutral atom of the element and then subtracting all of the non-bonding electrons on the atom (N_a) and half of the bonding electrons on the atom (B_a). The formal charge (FC_a) on atom A is, therefore, given by the following equation:

$$FC_a = V_a - N_a - \frac{B_a}{2} \tag{6.1}$$

Let us consider the example of sulphuric acid. It can be represented by the following Lewis structures, Structure I satisfies the octet rule while structure II violates it.

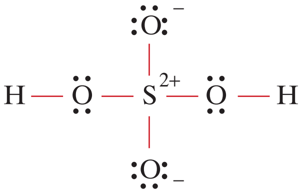


(Structure I)   (Structure II)

The formal charge on sulphur in Structure I can be calculated as: $FC_a = V_a - N_a - \frac{B_a}{2} = 6 - 0 - \frac{8}{2} = +2$

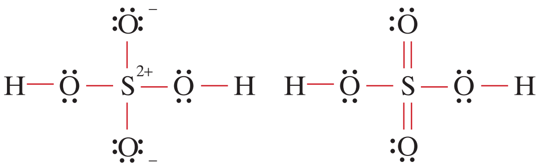
Let us also calculate the formal charges on the hydrogen and oxygen atoms in Structure I. An isolated H atom has one electron. In Structure I, each H has one bond and no unshared electrons. Therefore, formal charge on H = 1 – 0 – (2/2) = 0.

In Structure I, we also see that there are two kinds of oxygen atoms to consider. An isolated oxygen atom has six electrons, so the formal charge of oxygen also bonded to hydrogen = 6 – 4 – (4/2) = 0. For the oxygen atom not bonded to hydrogen, formal charge = 6 – 6 – (2/2) = –1. Non-zero formal charges are indicated in a Lewis structure by placing them alongside the atoms, as shown:



Note: The sum of the formal charges in the molecule is zero. It is useful to remember that, in general, the formal charges in any Lewis structure add up to the charge on the particle.

Similarly, calculating the formal charges in Structure II, for sulphur we have formal charge = 6 – 0 – (12/2) = 0, so the sulphur atom has no formal charge. The hydrogen and the oxygen atoms that are also bonded to S are the same in this structure as before, so they have no formal charges. And finally, the oxygen atoms that are not bonded to hydrogen have formal charge = 6 – 4 – (4/2) = 0. These oxygen atoms also have no formal charges. Now let us compare the two structures side by side.



(Structure I)   (Structure II)

The singly bonded structure on the left has a higher potential energy than the one with the double bonds since it involves separating negative charges from positive charges, which would require an increase in the potential energy. In general, the lower the potential energy of a molecule, the more stable it is.

Note: When several Lewis structures are possible, the one with formal charges closest to zero is the most stable and is preferred.

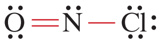
Formal charge has one other very useful application as it can help us decide whether a specific Lewis structure is legitimate or not. Just because we can write a structure that follows the octet rule does not necessarily mean that the structure actually represents the bonding in the molecule.

Solved Example 6-9

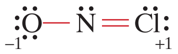
In nitrosyl chloride, determine whether the double bond exists between O and N or between N and Cl using the concept of formal charges.

Solution

We can write two resonance structures for the compound nitrosyl chloride:



No formal charge



Has formal charge

If both were important, we would expect both bonds to have double-bond character (i.e., length). In the structure on the left, there are no formal charges on the atoms. In the structure on the right, there is a formal charge of −1 on the oxygen and +1 on the chlorine. Recall that structures with the least amount of formal charge are most important in determining the actual bonding. Thus, the structure with the formal charge does not represent the actual bonding in the molecule. Experiments tell us that only the structure on the left, which has an N═O double bond and an N—Cl single bond, represents the bonding in NOCl.

Solved Example 6-10

Cyanogen $(CN)_2$ is known as a *pseudohalogen* because it has some properties similar to halogens. It is composed of two CN’s joined together. Do the two CN’s join through the carbon or the nitrogen (i.e., C

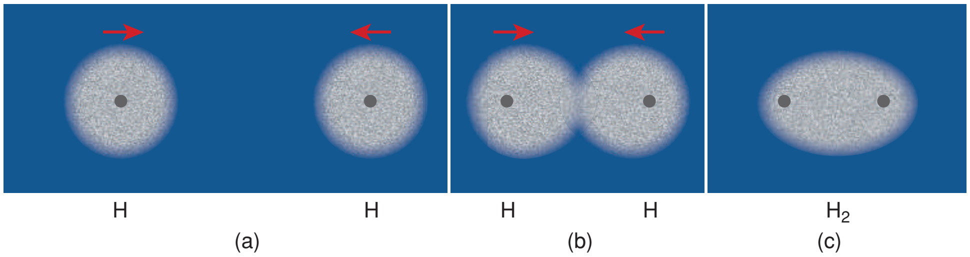


Figure 6.4 Formation of a covalent bond between two hydrogen atoms.

In the figure,

(a) Two H atoms separated by a large distance.

(b) As the atoms approach each other, their electron densities are pulled into the region between the two nuclei.

(c) In the H_2 molecule, the electron density is concentrated between the nuclei. Both electrons in the bond are distributed over both nuclei.

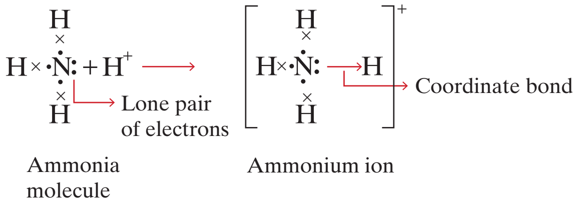
In the H_2 molecule, the buildup of electron density between the two atoms attracts both nuclei and pulls them together. Being of the same charge, however, the two nuclei also repel each other, as do the two electrons. In the molecule that forms, therefore, the atoms are held at a distance at which all these attractions and repulsions are balanced. Overall, the nuclei are kept from separating, and the net force of attraction produced by sharing the pair of electrons is called a **covalent bond**.

Every covalent bond is characterized by two quantities, the average distance between the nuclei held together by the bond, and the amount of energy needed to separate the two atoms to produce neutral atoms again. In the hydrogen molecule, the attractive forces pull the nuclei to a distance of 75 pm, and this distance is called the **bond length** (or sometimes the **bond distance**). Because a covalent bond holds atoms together, work must be done (energy must be supplied) to separate them. The amount of energy needed to "break" the bond (or the energy released when the bond is formed) is called the **bond energy**.

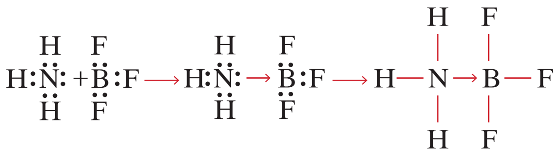
6.5 | COORDINATE OR DATIVE BONDING

During the formation of a bond by sharing of electrons between atoms, when both electrons of the shared pair are provided by one of the combining atoms, then the bond formed is called a *coordinate bond* or a *dative bond*. The atom which provides the electron pair is termed as the donor atom, while the atom which accepts it is termed as the acceptor atom. An arrow pointing from donor towards the acceptor atom represents a coordinate bond. Once a coordinate bond is formed, it cannot be distinguished from a normal covalent bond. Some examples of coordinate bond are:

1. **Formation of ammonium (NH_4^+) ion:** Here nitrogen is the donor atom, while H^+ is the acceptor ion as shown:



2. **Formation of coordinate bond between two molecules:** Sometimes, two or more stable molecules combine to form a molecular complex in which the constituent molecules are held together by a "coordinate bond". One typical example is the complex formed by coordinate bond between the molecules of NH_3 and BF_3.



Ammonia–boron
trifluoride complex

The nitrogen atom has a complete octet around it, but boron has only six electrons around it. The nitrogen atom donates its lone pair of electrons to boron so that it also acquires the octet. This sharing gives rise to a coordinate bond between N and B atoms.

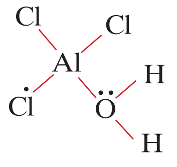
Solved Example 6-11

Which of the two, anhydrous or hydrated $AlCl_3$ is more soluble in diethyl ether? Justify using the concepts of bonding in not more than two or three sentences.

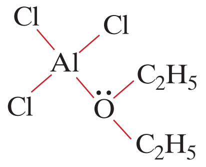
(IIT-JEE 2003)

Solution

Anhydrous $AlCl_3$ is more soluble in diethyl ether because the oxygen atom of the ether molecule donates its lone pair of electrons to the vacant orbital of electron deficient aluminium of $AlCl_3$ through coordinate bond formation. However, in case of hydrated $AlCl_3$, the aluminium atom is not electron deficient as the oxygen atom from the water molecule has already donated its electron pairs to fulfill the electron deficiency of Al.



Hydrated $AlCl_3$

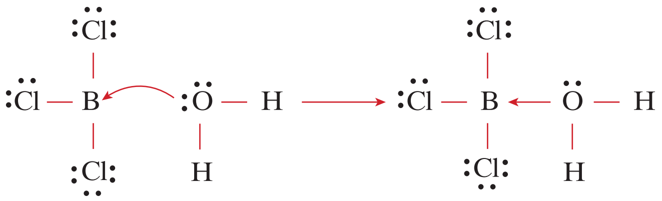


Anhydrous $AlCl_3$

Solved Example 6-12

BCl_3 has an incomplete valence shell. Use Lewis structures to show how it could form a coordinate covalent bond with a water molecule.

Solution



6.6 | VALENCE BOND THEORY

The valence bond (VB) theory was proposed by Heitler and London (1927) and further explained by Pauling *et al*. According to this theory, atoms with unpaired electrons tend to combine with other atoms which also have unpaired electrons. In this way, the unpaired electrons are paired up, and the atoms involved all attain a stable electronic arrangement. A covalent bond results from the pairing of electrons (one from each atom). The spins of the two electrons must be opposite (antiparallel) because of the Pauli exclusion principle that no two electrons in one atom can have all four quantum numbers the same.

The basic idea of the theory is that a *bond between two atoms is formed when* ***two electrons*** *with their* ***spins paired*** *are shared by two* ***overlapping*** *atomic orbitals, one orbital from each of the atoms joined by the bond*. By **overlap of orbitals** we mean that portions of two atomic orbitals from different atoms share the same space. This electron pair becomes concentrated in the region of overlap and helps bind the nuclei together. The amount that the potential energy is lowered when the bond is formed is determined in part by the extent to which the orbitals overlap.

The number of bonds formed by an atom is usually the same as the number of unpaired electrons in the ground state, that is, the lowest energy state. However, in some cases the atom may form more bonds than this. This occurs by excitation of the atom (i.e., providing it with energy) when electrons which were paired in the ground state are unpaired and promoted into suitable empty orbitals. This increases the number of unpaired electrons, and hence the number of bonds which can be formed. The shape of the molecule is determined primarily by the directions in which the orbitals point.

Orbital Overlap Concept

According to valence bond theory, a covalent bond is formed between two atoms in a molecule, when the half-filled valence atomic orbitals (AOs) of the two atoms containing unpaired electron overlap with one another and the electrons pair up in the overlap region. Due to the overlapping, electrons are localized between the atoms in the bond region. When the attractive forces (electron–nucleus of two different atoms) are stronger than the repulsive forces (electron–electron or nucleus–nucleus), energy is released; lowering of energy makes the molecule stable.

Types of Overlapping and Nature of Covalent Bonds

The following bonds are observed based on the type of overlapping. Covalent bonds are classified into two main types – *sigma* (σ) bonds and *pi* (π) bonds.

1. **σ bond:** It is formed by head-on overlap of orbitals. In a σ covalent bond, the region of overlap of atomic orbitals lies along the line joining the two nuclei coming together and the electron density is concentrated in this region. Different types of overlap for σ bonds:
   - **(a)** *s*–*s* overlap, such as in H_2 molecule [Fig. 6.5(a)].
   - **(b)** *s*–*p* overlap, such as in HX molecule (X = F, Cl, Br, I) [Fig. 6.5(b)].
   - **(c)** *p*–*p* overlap, such as in X_2 molecule (X = F, Cl, Br, I) [Fig. 6.5(c)].

   Keeping the internuclear distance same, the relative strength of bond resulting from three kinds of overlap is:

$$s\text{–}s < s\text{–}p < p\text{–}p$$

   The order of bond strength can be explained on the basis of the fact that more the area of overlap, higher will be the strength. Since the *p* orbital has directional property, *p*–*p* overlap provides more area for overlap for the same internuclear distance.

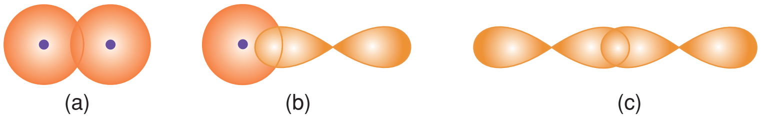


Figure 6.5 Different types of overlaps in σ bond: (a) *s*–*s* overlap; (b) *s*–*p* overlap and (c) *p*–*p* overlap.

Note: The shape of the molecule is determined by the σ bonds (and lone pairs) but not by the π bonds.

2. **π bond:** It is formed by sideways overlap of orbitals and it merely shortens the bond length (Fig. 6.6). In a π covalent bond, the region of overlap of atomic orbitals lies parallel to the line joining the two nuclei coming together, both above and below the axis.

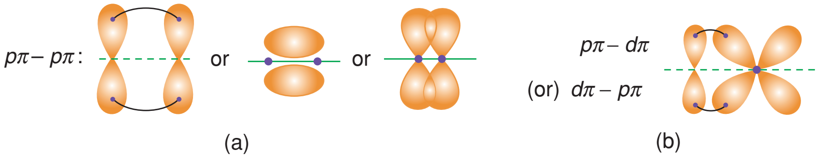


Figure 6.6 Different types of overlap for π bonds.

The relative strength of the π bonds increases when the intermolecular distance increases and the order is:

$$2p\pi\text{–}2p\pi > 2p\pi\text{–}3d\pi > 2p\pi\text{–}3p\pi > 3p\pi\text{–}3p\pi$$

The **strength of the bond** depends on the extent of overlap between the orbitals participating in the bond formation. In case of σ bond between *s* or *p* orbitals, the overlap is cylindrical about the bond axis; whereas in case of π bond, the *p* orbitals overlap above and below the bond axis. The sideways overlap is weaker than that about the axis. The π bond is thus weaker than the σ bond. Also, π bond is always formed in addition to the σ bond in molecules, particularly those containing multiple bonds.

The valence bond theory also explains the **directional properties** of the bonds formed in terms of overlap and hybridization (explained later) and hence account for the geometry of the resulting molecules. Because the strength of the bond depends upon the extent of overlap, orbitals (apart from *s* orbitals) bond only in certain directions to obtain maximum overlap. Consider the formation of molecule hydrogen sulphide, H_2S. Experiments have shown that it is a non-linear molecule in which the H

Bonding as an Overlap of Atomic Orbitals

According to valence bond theory when two atoms come close together for bond formation, their atomic orbitals overlap. The overlap may be positive, negative or have a net zero value depending upon the orientation of the overlapping orbitals. The various arrangements that can result from overlap between *s* and *p* orbitals are depicted in Fig. 6.7.

The atomic orbital overlap is the key feature that explains the bond formation between diatomic (homonuclear and heteronuclear) and polyatomic molecules.

In polyatomic molecules, the overlap and the orientation of the resulting orbitals also determines the shapes of molecules. For example, we know the shapes of polyatomic molecules such as CH_4, NH_3 and H_2O to be tetrahedral, pyramidal and bent on the basis of VSEPR theory. We will now see if the valence bond theory would account for these geometries on the basis of overlap between atomic orbitals.

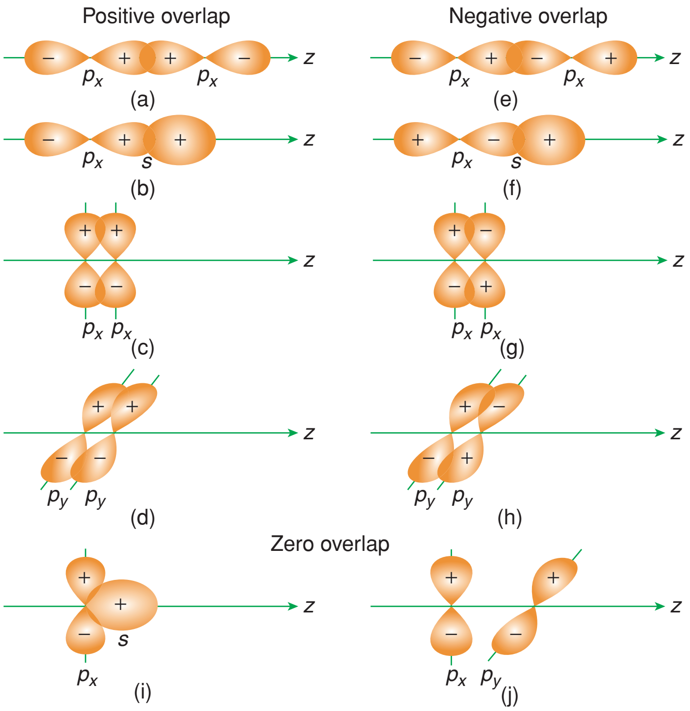
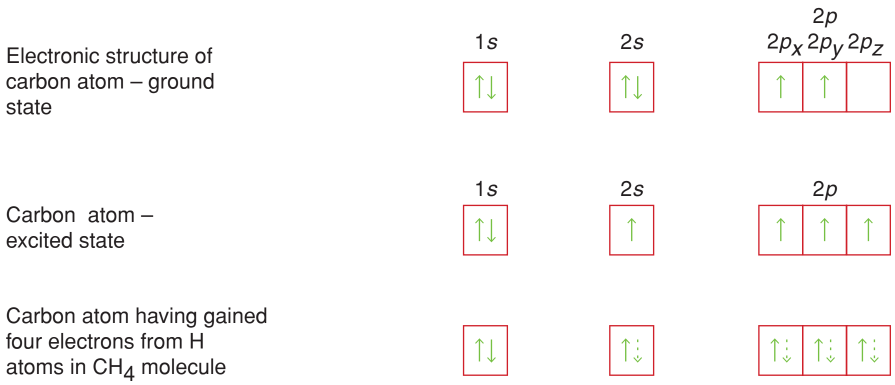


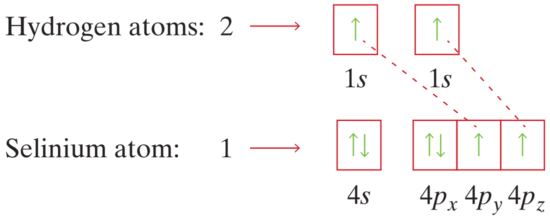
Figure 6.7 The positive, negative and zero overlap of *s* and *p* orbitals.

Let us consider the formation of methane molecule. The C atom in its ground state has the electronic configuration $1s^2$, $2s^2$, $2p_x^1$, $2p_y^1$ and only has two unpaired electrons, and so can form only two bonds. If the C atom is excited, then the 2*s* electrons may be unpaired, giving $1s^2$, $2s^1$, $2p_x^1$, $2p_y^1$, $2p_z^1$. There are now four unpaired electrons which overlap with singly occupied *s* orbitals on four H atoms.

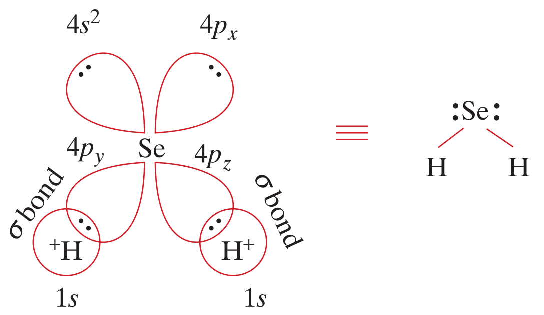

Electronic structure of carbon atom – ground state
Carbon atom – excited state
Carbon atom having gained four electrons from H atoms in CH_4 molecule
1*s*
2*s*
2*p*
2p_x 2p_y 2p_z

The shape of the CH_4 molecule is not immediately apparent. The three p orbitals p_x, p_y and p_z are mutually at right angles to each other, and the s orbital is spherically symmetrical. If the p orbitals were used for bonding, then the bond angle in water should be 90°. Using similar argument, we can show that the bond angles in NH_3 and H_2O should also be 90°. The bond angles actually found differ appreciably from these:

CH_4 H



When H_2Se molecule is formed, 1*s* atomic orbital of two hydrogen atoms overlaps with two half-filled $4p_y$ and $4p_z$ orbitals of selenium atom to form σ bond. There are two lone pairs of electrons present on the selenium atom.



6.7 | HYBRIDIZATION

In 1931, L. Pauling proposed that the different atomic orbitals in the valence shell of the same atom combine or mix with each other resulting in more stable set of orbitals called **hybridized orbitals**. This process is known as *hybridization*.

Mathematically, the wave functions of the electrons in the orbitals of an atom are combined to give sets of equivalent wave functions called **hybridized atomic orbitals**. Hybridization is a simple mathematical process used for modifying electron densities, for describing bonding geometries and electron densities in more complex molecules. The driving force for hybridization is the formation of a bonding geometry with the lowest net potential energy, which is accessible by energetically feasible means.

Hybridization results in a set of atomic orbitals which have equal energies (degenerate) and are intermediate between those of the basic orbitals used to construct them. These hybridized atomic orbitals can overlap more effectively with the atomic orbitals of other atoms in the molecule, thus providing an overall molecular structure which has stronger bonds and lower energy. The other inner atomic orbitals which are not used in constructing the hybrid orbitals remain unaffected by the hybridization process.

Note: *Hybridization is not a physical phenomenon*; it is merely a *mathematical operation* that combines the atomic orbitals in such a way that the new (hybrid) orbitals possess the geometrical properties, etc., that are reasonably consistent with observations in a wide range (but not in all) of molecules.

Salient Features of Hybridization

The important features of hybridization are as follows:

1. The number of hybridized orbitals formed is equal to the number of atomic orbitals that get hybridized.
2. The hybridized orbitals are always equivalent in energy and shape. For example, one *s* orbital and three *p* orbitals are mixed to form four sp^3 hybrid orbitals, which are of equal energy; and each sp^3 hybrid orbital has 25% *s* character and 75% *p* character. For different hybridizations possible of *s*, *p* and *d* orbitals, the percentages of *s*, *p* and *d* characters are given in Table 6.2
3. The atomic orbitals involved in hybridization can be empty, half-filled or completely filled.
4. The hybridized orbitals have two lobes, one larger and one smaller (Fig. 6.8); larger lobes are more effective in overlapping with other atomic orbitals and forming stable bonds. Smaller lobes are generally not shown since they are close to nucleus and do not effectively participate in bond formation.
5. The hybridized orbitals are directed in certain directions in space which will have stable arrangements. The type of hybridization gives the geometry of the molecule.
6. Hybridized orbitals are usually involved only in σ bonds; π bonds involve the overlap of unhybridized orbitals.

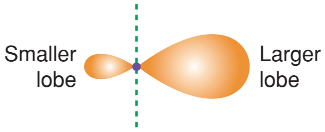


Figure 6.8 Shape of hybrid orbital.

7. Hybridization is not invoked in isolated atoms, only in covalent bond formation with other atoms.

Table 6.2 Percentage of *s*, *p*, *d* characters in various hybridized orbitals

Hybridization type	% *s*	% *p*	% *d*
sp	50	50	–
sp^2	33.33	66.67	–
sp^3	25	75	–
sp^3d	20	60	20
sp^3d^2	~16.5	50	~33
sp^3d^3	~14	~43	~43

Note:

(a) As the %*s* character increases in a hybrid orbital, the hybrid orbital becomes bulkier and shorter. On the other hand, as the %*p* or %*d* character increases, the orbital becomes longer and thinner (Fig. 6.9).

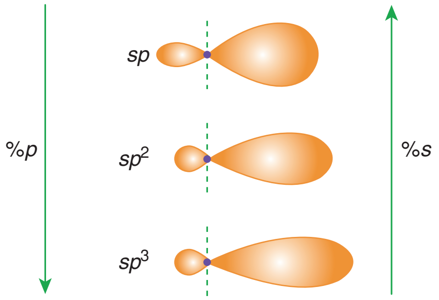


Figure 6.9 Shape of hybrid orbitals with increasing *p* character.

(b) As the %*s* character increases, the energy of the hybrid orbital decreases and as the %*p* or %*d* character increases, the energy of the hybrid orbital increases.

Some important conditions for hybridization are:

1. Only the orbitals present in the valence shell undergo hybridization.
2. For effective hybridization, the energy of mixing orbitals must nearly be the same.
3. Promotion of electrons to empty orbitals is not a necessary step in hybridization.
4. It is not essential that only half-filled orbitals take part in hybridization. In some cases, even filled orbitals of the valence shell participate in hybridization.

The possible combinations of orbitals for making a hybrid orbital are listed as follows:

1. $sp = s$ + any p orbital
2. $sp^2 = s$ + any two p orbitals
3. $sp^3 = s + p_x + p_y + p_z$
4. $sp^3d = s + p_x + p_y + p_z + d_{z^2}$ (Trigonal bipyramidal)
5. $sp^3d = s + p_x + p_y + p_z + d_{x^2-y^2}$ (Square pyramidal)
6. $dsp^3 = (n-1)d_{x^2-y^2} + ns + np_x + np_y$
7. $sp^3d^2 = ns + np_x + np_y + np_z + nd_{x^2-y^2} + nd_{z^2}$
8. $d^2sp^3 = (n-1)d_{x^2-y^2} + (n-1)d_{z^2} + ns + np_x + np_y + np_z$

9. $sp^3d^3 = ns + np_x + np_y + np_z + nd_{x^2-y^2} + nd_{xy} + nd_{z^2}$
10. $d^3s = (n-1)d_{xy} + (n-1)d_{xz} + (n-1)d_{yz} + ns$ (Tetrahedral)

Calculation of Steric Number

Steric number is the number of atoms bonded to the central atom of a molecule plus the number of lone pairs on central atom. This number is used to determine the shape of molecules. The following steps can be followed to find the steric number of any molecule.

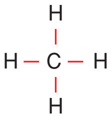
1. Identify one central atom.
2. Calculate the total number of σ bonds (n_1) formed by the central atom + number of lone pair of electrons (n_2) on the central atom to find the steric number.

   Steric Number (S.N.) = $n_1 + n_2$

   This is illustrated with the following examples in which the steric number of the underlined central atom is determined.

   (a) For carbon in methane

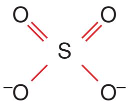
$\underline{C}H_4$



Number of σ bonds with C = 4
Number of lone pairs on C = 0
Therefore, steric number = 4 + 0 = 4

(b) For sulphur in sulphate ion

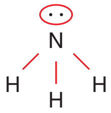
$\underline{S}O_4^{2-}$



Number of σ bonds with S = 4
Number lone pairs on S = 0
Therefore, steric number of S = 4 + 0 = 4

3. For nitrogen in ammonia

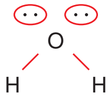
$\underline{N}H_3$



Number of σ bonds with N = 3
Number of lone pairs = 1
Therefore, steric number of N = 3 + 1 = 4

(d) For oxygen in water

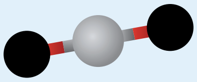
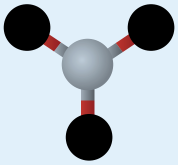
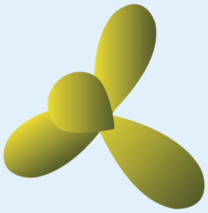
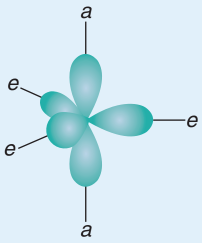
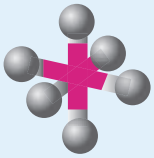
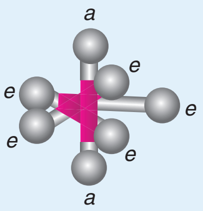
$H_2\underline{O}$



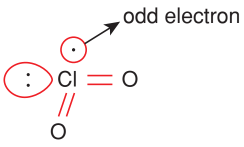
Number of σ bonds with O = 2
Number of lone pairs on O = 2
Therefore, steric number of O = 2 + 2 = 4

The relation between steric number, hybridization and shape of molecules is listed in Table 6.3.

Table 6.3 Relation between steric number, hybridization and shape of molecules.

Steric number	Hybridization	Orientation of the hybrid orbital in space or electronic geometry around the central atom	Angles between hybrid orbitals
2	*sp*	Linear 	180°
3	sp^2	Trigonal planar 	120°
4	sp^3	Tetrahedral (Td) 	109°28´
5	sp^3d	Trigonal bypyramidal (TBP) 	Axial (*a*) and equatorial (*e*): 90° *e* and *e*: 120° *a* and *a*: 180°
6	sp^3d^2	Octahedral (Oh) 	Between two adjacent orbitals: 90° Between two Opposite orbitals: 180°
7	sp^3d^3	Pentagonal bipyramidal (PBP) 	*a* and *a*: 180° *a* and *e*: 90° *e* and *e*: 72°

Note: During calculation of steric number in odd electron molecules, consider odd electron as a lone pair. For example, in ClO_2



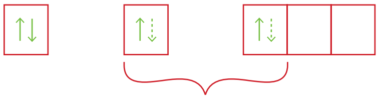
The steric number = $\underset{(\sigma\text{-bonds})}{2} + \underset{(\text{lone pair})}{1} + \underset{(\text{odd electron})}{1} = 4$

Some Examples of Hybridization

The various types of hybridization involving *s*, *p* and *d* orbitals are as follows:

1. ***sp* hybridization:** The hybridization of one *s* orbital and one *p* orbital on a central atom gives rise to two equivalent *sp* hybrid orbitals. Generally the p_z orbital is involved in overlap with *s* orbital and the hybrid *sp* orbital has 50% *s* and 50% *p* character. The two hybridized *sp* orbitals are in a linear arrangement, that is, 180° apart as shown in Fig. 6.10 using BeF_2 as an example. If bonds are formed by the overlap of these hybrids with orbitals of other atoms, then the other atoms will occupy positions on opposite sides of this central atom. Because of their shape, these *sp* orbitals overlap more effectively and result in stronger bonds than the original atomic orbitals. This type of hybridization is also known as diagonal hybridization.

BeF_2 molecule having gained a share in two electrons by bonding of two F atoms



sp hybridization of the two orbitals in the outer shell, hence structure is linear

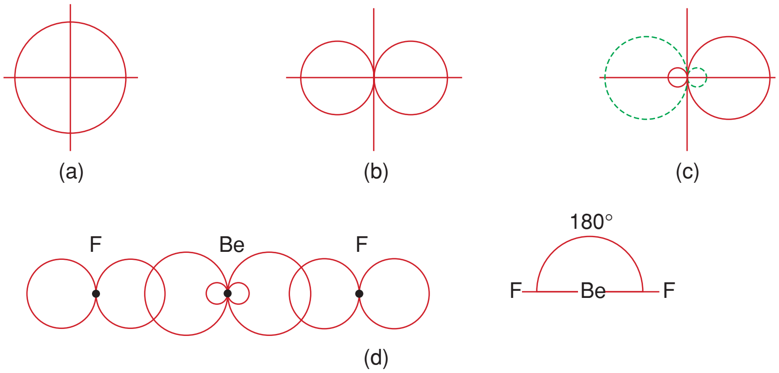
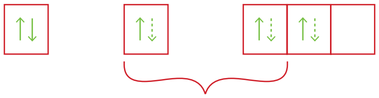


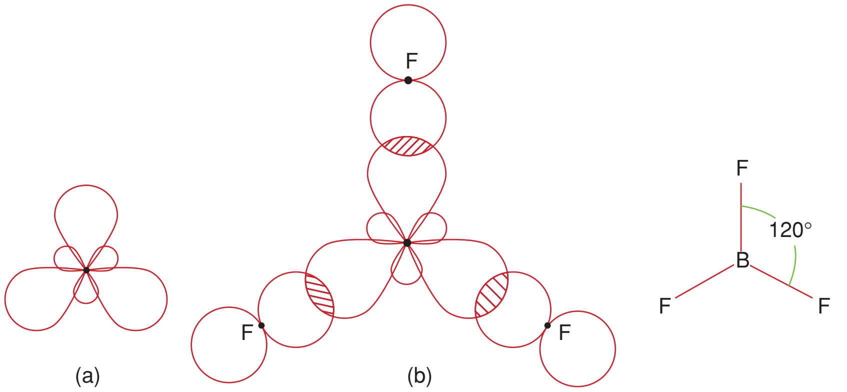
Figure 6.10 (a) *s*-orbital, (b) *p*-orbital, (c) formation of two *sp* hybrid orbitals and (d) their use in forming beryllium difluoride.

2. ***sp*^{2} hybridization:** The hybridization of one *s* orbital and two *p* orbitals of a central atom gives rise to three sp^2 orbitals, for example, BF_3 (Fig. 6.11). These three orbitals are equivalent, and repulsion between them is minimized if they are distributed at 120° to each other giving a planar triangle. In the hybrid orbitals, one lobe is bigger than the other, so it can overlap more effectively and hence form a stronger bond than the original atomic orbitals. The three sp^2 hybridized orbitals are trigonal and planar, 120° apart.

BF_3 molecule having gained a share in three electrons by bonding of three F atoms



sp^2 hybridization of the three orbitals in outer shell, hence structure is a planar triangle

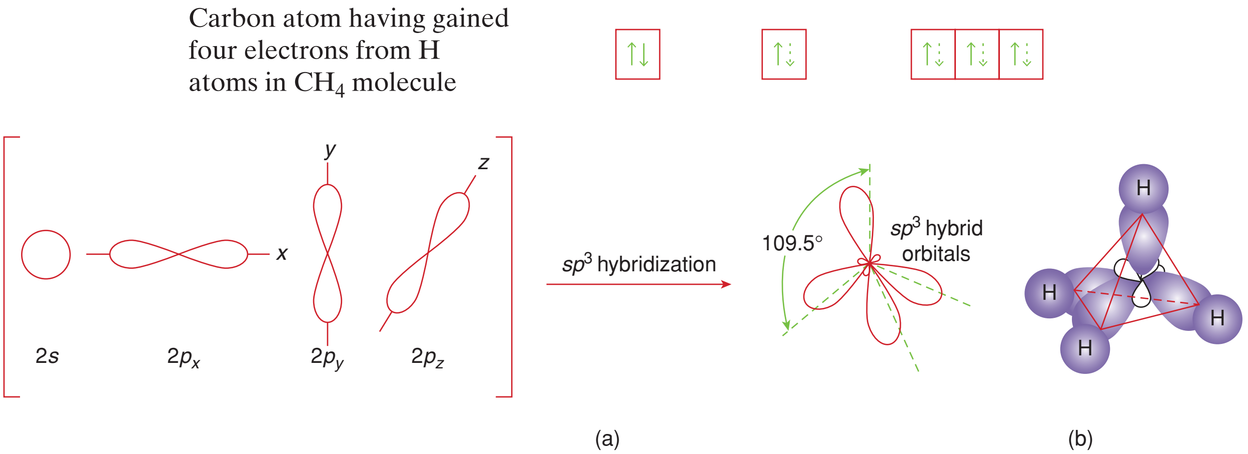


(a) (b)

Figure 6.11 (a) sp^2 hybrid orbitals and (b) the BF_3 molecule.

3. **sp^3 hybridization:** Mixing one *s* and all three *p* atomic orbitals produces a set of four equivalent sp^3 hybridized atomic orbitals. The four sp^3 hybrid orbitals having 75% *p* character and 25% *s* character point towards the vertices of a tetrahedron. Placement of the four orbitals in tetrahedral geometry provides the maximum separation between the electron pairs and minimizes electronic repulsion.

   When sp^3 hybridized orbitals are used by the central atom in the formation of molecule, the molecule acquires the shape of a tetrahedron An important example of this bond type is methane, CH_4. In the free carbon atom, there are two unpaired electrons in separate 2*p* orbitals. The single 2*s*, and the three 2*p* orbitals of carbon mix into four sp^3 hybrid orbitals which are chemically and geometrically identical (Fig. 6.12). The four sp^3 orbitals of carbon atom overlap with 1*s* orbitals of four hydrogen bonds to produce four σ bonds.

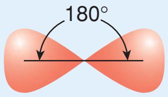
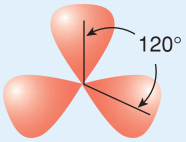
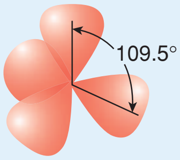


(a) (b)

Figure 6.12 (a) sp^3 hybrid orbitals and (b) bonding in CH_4 molecule.

In case of ammonia and water, the hybridization is sp^3; but the observed H

Table 6.4 Directional properties of hybrid orbitals formed from *s* and *p* atomic orbitals

Hybridization	*sp*	sp^2	sp^3
Shape	 Linear	 Planar triangular	 Tetrahedral

Hybridization in Ethane, Ethene and Ethyne

1. **sp^3 hybridization in C_2H_6:** The structure of ethane and bonding in ethane is similar to that for methane as both the carbon atoms undergo sp^3 hybridization. Of the four sp^3 hybrid orbitals on each carbon, three overlap with *s* orbitals of three hydrogen atoms to form s–sp^3 σ bonds. The fourth sp^3 hybrid orbital on each carbon overlaps axially to form sp^3–sp^3 σ bond. The C

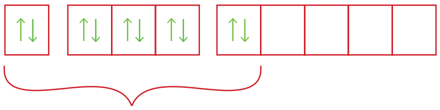
bond. Finally, the remaining unhybridized $2p$ orbitals, one from each carbon atom, overlap to produce a π bond, which accounts for the second bond of the double bond. The C take part in hybridization and account for geometries such as trigonal bipyramidal and octahedral. The energy of 3*d* orbitals is similar to the energy of both 3*s* and 3*p* orbitals and 4*s* and 4*p* orbitals; and can thus be involved in hybridization with both. The type of hybridization possible with *s*, *p* and *d* orbitals along with their geometries and some examples are given in Table 6.6.

Table 6.6 Types of hybridization of orbitals and their geometries

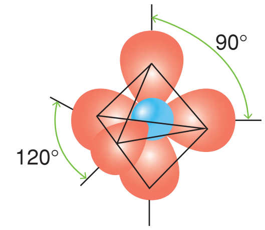
Type of hybridization	Number of atomic orbitals involved	Shapes of molecules	Examples
dsp^2	$4\ [d + s + p(2)]$	Square planar	$[Ni(CN)_4]^{2-}$
sp^3d	$5[s + p(3) + d]$	Trigonal bipyramidal	PF_5, PCl_5
sp^3d^2	$6[s + p(3) + d(2)]$		
sp^3d^2	$6[s + p(3) + d(2)]$ or $[d(2) + s + p(3)]$	Octahedron	SF_6,$[CoF_6]^{3-}$ $[Co(NH_3)_6]^{3+}$
sp^3d^3	$7[s + p(3) + d(3)]$	Pentagonal bipyramidal	IF_7

1. **Formation of PCl_5 by sp^3d^2 hybridization:** The bonding in PCl_5 may be described using hybrids of the 3*s* 3*p* and 3*d* atomic orbitals for P. Hybridization of one *s*, three *p* and one *d* atomic orbitals produce five sp^3d hybrid orbitals, which are trigonal bipyramidal in shape. These hybrid orbitals overlap with singly occupied *p* orbitals of chlorine to form five σ bonds.

Phosphorus having gained five electrons
from chlorine atoms in PCl_5 molecule

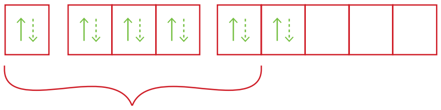


sp^3d hybridization, trigonal bipyramidal shape

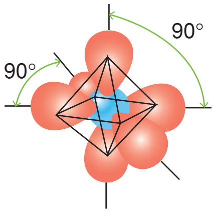


The P

Sulphur atom having gained six electrons from fluorine atoms in SF_6 molecule



sp^3d^2 hybridization, octahedral shape



Solved Example 6-16

On the basis of hybridization, explain the shape of sulphur tetrafluoride.

Solution

In SF_4 molecule, the central atom, sulphur, has the outer electron configuration $3s^2\, 3p_x^2\, p_y^1\, p_z^1$ as shown above in the formation of SF_4 molecule, sulphur needs four half-filled orbitals to overlap with 3*p* orbitals of four fluorine atoms. This happens by the unpairing of the two p_x electrons and movement of one of them into one of the 3*d* orbitals on the excitation of atom. These five orbitals hybridize to give sp^3d hybrid orbitals of equivalent energy. The central atom is therefore surrounded by five hybrid orbitals. One of these contains a lone pair of electrons while the other four contain one unpaired electron each, which overlap with *p*-orbitals of fluorine atoms to form S

1. If there are two pairs of electrons in the valence shell of the central atom, the orbitals containing them will be oriented at 180° to each other. It follows that if these orbitals overlap with orbitals from other atoms to form bonds, then the molecule formed will be linear.
2. If there are three electron pairs on the central atom, they will be at 120° to each other, giving a plane triangular structure.
3. For four electron pairs the angle is 109.5°, and the shape is tetrahedral.
4. For five pairs, the shape is a trigonal bipyramid.
5. For six pairs, the angles are 90° and the shape is octahedral.

Nyhlom and Gillespie took into consideration the differences in behavior of the bonding and non-bonding electron pairs to further enhance the VSEPR model. The main postulates of VSEPR theory are:

1. The shape of the molecule is determined by repulsions between all of the electron pairs present in the valence shell (including bonding and non-bonding).
2. The electron pairs in the valence shell experience electrostatic repulsions due to negatively charged electron clouds.
3. The electron pairs tend to occupy positions that minimize these repulsions. If the valence shell can be visualized like a sphere, then the electron pairs are localized on the spherical surface at maximum distance from each other.
4. A multiple bond (double or triple) is treated like a single bond and the electron pairs (2 or 3) involved in multiple bonding are treated as single super pair. This is only a qualitative approximation. In reality, double bonds cause more repulsion than single bonds, and triple bonds cause more repulsion than a double bond. The double bond needs more space as compared to the single bond. The repulsion order in relation to the bonds is as follows:

   Double bond–double bond > Double bond–single bond > Single bond–single bond

5. If a molecule has two or more resonance structures, then VSEPR model can be applied to any one structure. Formal charges are not included in the representation.
6. The magnitude of repulsions between bonding pairs of electrons depends on the electronegativity difference between the central atom and the other atoms.
7. A lone pair (non-bonded electron pair) of electrons takes up more space round the central atom than a bond pair, since the lone pair is attracted to one nucleus whilst the bond pair is shared by two nuclei. It follows that repulsion between two lone pairs is greater than repulsion between a lone pair and a bond pair, which in turn is greater than the repulsion between two bond pairs. Thus, the presence of lone pairs on the central atom causes slight distortion of the bond angles from the ideal shape. If the angle between a lone pair, the central atom and a bond pair is increased, it follows that the actual bond angles between the atoms must be decreased. The repulsion will be:

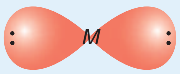
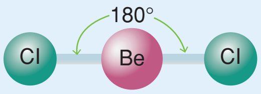
   Lone pair–lone pair > Lone pair–bond pair > Bond pair–bond pair

8. Sometimes, the lone pair may be transferred from filled shell of an atom to unfilled shell of the adjacent bonded atom. This phenomenon of transferring electron is known as "back bonding".

Molecular Geometry Based on Number of Electron Pairs

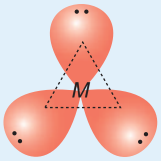
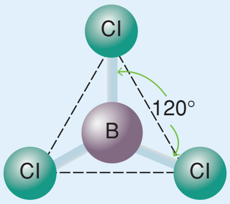
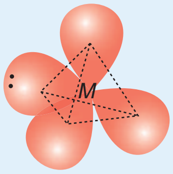
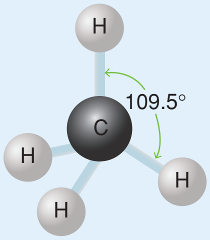
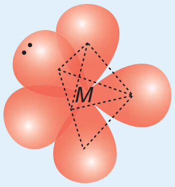
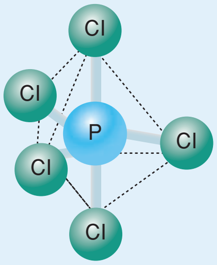
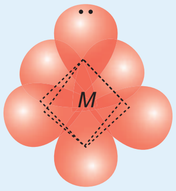
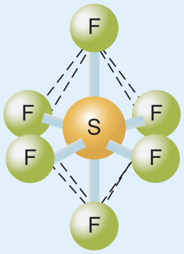
For sake of simplicity, let us only consider molecules made up of two types of elements A and B. Then the molecules will have the general formula, AB_x, where $x = 1, 2, 3 \ldots$ Table 6.7 gives some examples of such molecules, along with the number of lone pairs, their arrangement and geometry.

Table 6.7 Molecules with the number of electron pairs, their arrangement and geometry

Number of electron pairs	Shape	Example
2	 Linear	$BeCl_2$ 

(Continued)

Table 6.7 (Continued)

Number of electron pairs		Shape	Example	
3		Planar triangular	BCl_3	
4		Tetrahedral (It is pyramid shaped with four triangular faces and four corners)	CH_4	
5		Trigonal bipyramidal (It consists of two three-sided pyramids joined by sharing a common face – the triangular plane through the center.)	PCl_5	
6		Octahedral (It is an eight-sided figure with six corners. It consists of two square pyramids that share a common square base.)	SF_6	

Molecular Geometry in Presence One or More Lone Pairs on Central Atom

In view of the fact that the presence of a lone pair can considerably affect the geometry of the molecule, determination of geometry of molecules with one or more lone pair is somewhat more complicated**.** There are three types of repulsive forces operative and these are between bonding pairs, between lone pairs and between bonding and lone pairs in the following order:

Lone pair–Lone pair > Lone pair–Bond pair > Bond pair–Bond pair

(Here bond pair refers to a single bond.)

Such molecules can be represented as AB_xL_y, where A is the central atom, B is the surrounding atom and L represents the electron pairs. Both x and y are integers with values 1, 2, 3… and indicate the number of atoms and lone pairs surrounding the central atom. Some examples of the molecules with central atom having one or more lone pairs along with their geometries are discussed with the following examples.

Note: Molecular shape describes the arrangement of atoms, not the arrangement of electron pairs.

Some Examples of Effect of Lone Pairs on the Shape of the Molecules

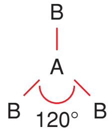
The lone pair will distort the perfect geometry of hybrid orbitals which is observed in absence of anylone pair. Different cases illustrated the effect of lone pair on molecular geometry are illustrated as follows.
(Here, A, B = atoms, L = lone pair.)

Case 1: Steric number = 2, hybridization = *sp* and shape is linear.
Molecules of the type AB_2 (e.g. BeH_2)

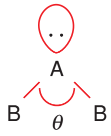
$$B - A - B$$

Case 2: Steric number = 3, hybridization = sp^2.

(a) Molecules of the type AB_3 (e.g., $AlCl_3$, CO_3^{2-}): The bond angle θ is 120° and shape is trigonal planar.

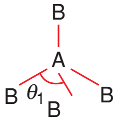


(b) Molecules of type AB_2L (e.g., SO_2, NO_2^-): The bond angle θ is less than 120° because bond pair(bp)-bond pair(bp) repulsion is less that bond pair(bp)-lone pair (lp) repulsion. So the molecule is V-shaped.

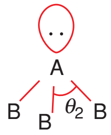


Case 3: Steric number = 4, hybridization = sp^3

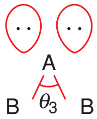
(a) Molecules of the type AB_4 (e.g., CH_4): The bond angle θ_1 is 109°28′ and the shape is regular tetrahedral.



(b) Molecules of the type AB_3L (e.g., NH_3): The bond angle $\theta_2 < \theta_1 = 109°28'$. Thus, the shape is distorted tetrahedral.

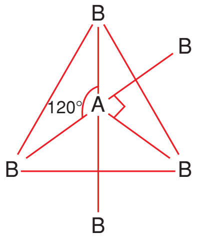


(c) Molecule of the type AB_2L_2 (e.g., H_2O): The bond angle $\theta_3 < \theta_2 < \theta_1 = 109°28'$. The molecule is V-shaped.



Case 4: Steric number = 5, hybridization = sp^3d.

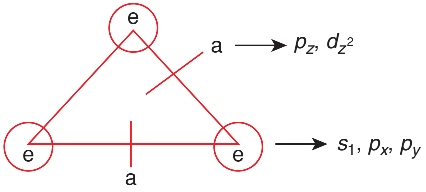
(a) Molecules of the type AB_5: The bond angles are 120° and 90° and the molecular geometry is trigonal bipyramidal.



Before we go ahead, let's examine the hybridization sp^3d. In sp^3d hybridization, there are two positions available:

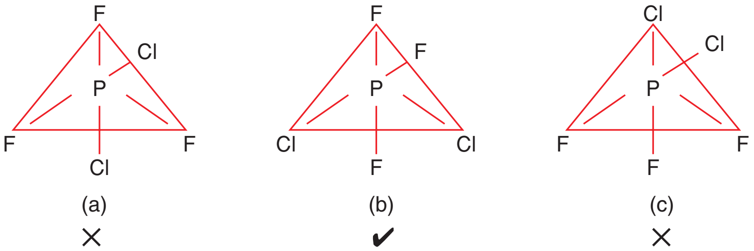
(i) Axial positions: These positions are at an angle of 90° to the plane. They are made by p_z and d_{z^2} orbitals

(ii) Equatorial positions: These are the three positions which are forming the plane and are at angle of 120° with each other. They are made by s_1, p_x and p_y orbitals.



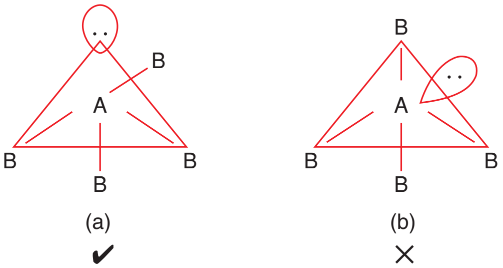
Therefore, equatorial positions have more *s*-character than the axial positions. Also, as % of *s* character increases, electronegativity increases. Thus, equatorial positions are more electronegative than axial positions.

Note: According to **Bent's rule**, in trigonal bipyramidal geometry, the more electronegative element should go to the less electronegative position (i.e., axial position) and less electronegative element should go the more electronegative position (i.e., equatorial position) to minimize the overall repulsion in the molecule. For example, consider the following structures, for PCl_2F_3



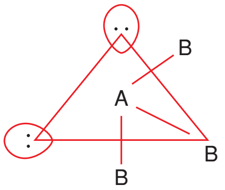
In the above structures, (b) is correct according to Bent's rule because more electronegative F is at the axial position and less electronegative Cl is at the equatorial position.

(b) Molecules of the type AB_4L (e.g., SF_4, XeO_2F_2): The shape of the molecule is seesaw.

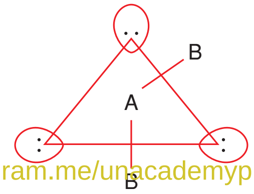


In the above structures, (a) is correct as in trigonal bipyramidal geometry, the lone pair will always go to equatorial position to minimize lp-lp and bp-bp repulsion.

(c) Molecules of the type AB_3L_2(BrF_3, XeF_3^+): The molecular geometry is T-shaped.

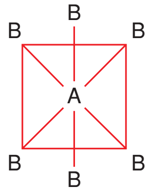


(d) Molecules of the type AB_2L_3(e.g., ICl_2^-, $[I(CN)_2]^-$, I_3^-, XeF_2): The shape of the molecules is linear.

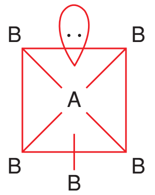


Case 5: Steric number = 6, hybridization is sp^3d^2.

(a) Molecules of the type AB_6 (e.g., SF_6, $TeCl_6$, XeO_6^{4-}): The shape of the molecules is octahedral.

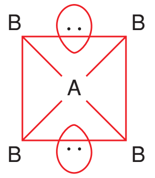


(b) Molecules of the type AB_5L (e.g., IF_5, XeF_5^+): The geometry of the molecule is distorted octahedral or square pyramidal.



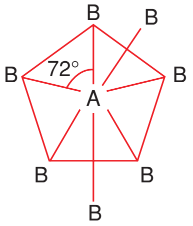
Note: In octahedral geometry, all positions are equivalent, so lone pair can be put anywhere.

(c) Molecules of the type AB_4L_2(e.g., XeF_4, $[ICl_4]^-$): The shape of the molecules is square planar.

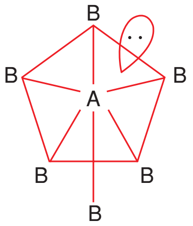


Case 6: Steric number = 7, hybridization = sp^3d^3.

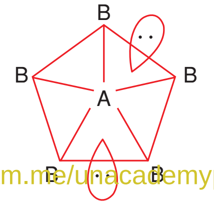
(a) Molecules of the type AB_7(e.g., IF_7): The shape of the molecule is pentagonal bipyramidal and bond angle = 72°, 90°



(b) Molecules of the type AB_6L (e.g., XeF_6, IF_6^-): The shape of the molecules is distorted octahedral.

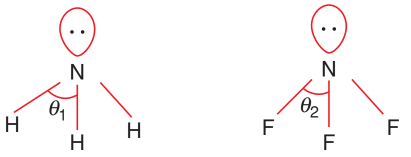


(c) Molecules of the type AB_5L_2 (e.g., $[XeF_5]^-$): The shape of the molecule is pentagonal planar.



Some Examples of Effect of Electronegativity on Molecular Geometry

Let us consider the following examples to understand the effect of electronegativity on geometry of molecules.
Observation: NH_3 has a bond angle = 107° but NF_3 has a bond angle = 102°.
Explanation: Consider the following structures for the given molecules.

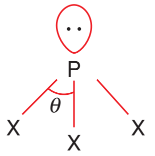


(a) (b)

In structure (a), the bond pair of N–H bond is more towards N; it being more electronegative than H. However in structure (b), the bond pair of N–F bond is shifted more towards F because F is more electronegative than N; therefore, $\theta_1 > \theta_2$. The difference in bond angles of H_2O and F_2O can also be explained on similar basis.

Note: In absence of lone pair, electronegativity does not matter. For example, CH_4 and CF_4 or SiH_4 and SiF_4 have the same bond angles.

Observation: The trend in bond angles: $PI_3 > PBr_3 > PCl_3 > PF_3$
Explanation: Consider the following structure for the molecules.



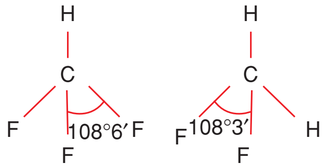
X = F, Cl, Br, I

In the given series, the bond angle decreases as we go from I to F due to steric crowding. As the size of X increases, repulsion increases and thus θ increases.

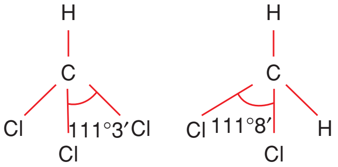
Size of halogen atoms: I > Br > Cl > F

Therefore, order of bond angle: $PI_3 > PBr_3 > PCl_3 > PF_3$

Observation: Bond angle ($\widehat{\text{CFF}}$) of $CHF_3 > CH_2F_2$ (i.e., 108°6′ > 108°3′)
Explanation: This can be explained on the basis of Bent's rule which states that more electronegative element prefers to stay in orbital having more *p*- character and further, it can also increase the *p*- character in its attached orbital from the central atom depending upon the circumstance.



Note: This is not applicable in $CHCl_3$ and CH_2Cl_2 as bond angle increases due to larger size of Cl atoms.



Note: Also as *p*-character increases, bond length will increase whereas an increase in *s*-character will shorten the bond length. For example,

(i) $d_{\text{N-N}}$ in $N_2H_4 > d_{\text{N-N}}$ in N_2F_4
(ii) $d_{\text{C-C}}$ in $C_2H_6 > d_{\text{C-C}}$ in C_2F_6
(iii) $d_{\text{O-O}}$ in $O_2H_2 > \text{d}_{\text{O-O}}$ in O_2F_2
(iv) $\text{d}_{\text{C-Cl}}$ in $CH_3Cl > d_{\text{C-Cl}}$ in CF_3Cl

Drago's Rule

According to Drago's Rule, if the central atom is in third row or below in the periodic table, then the lone pair will occupy a stereochemically inactive *s* orbital and thus pure "*p*" orbitals would participate in bonding. In such a case, bond angle would be nearly 90° if the electronegativity of the surrounding atom ≤ 2.5. For example, consider the following series for bond angles.

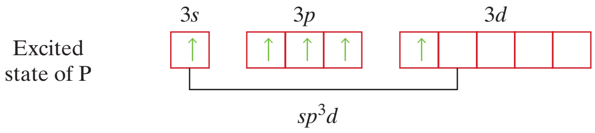
$$\begin{array}{cccc} NH_3 > & PH_3 > & AsH_3 > & SbH_3 \\ 107^\circ & 93.8^\circ & 91.8^\circ & 91.3^\circ \\ H_2O > & H_2S > & H_2Se > & H_2Te \\ 104.5^\circ & 92^\circ & 91^\circ & 89.5^\circ \end{array}$$

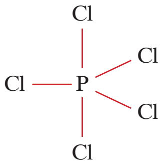
Solved Example 6-17

Using VSEPR theory deduce the structures of PCl_5 and BrF_5. **(IIT-JEE 2004)**

Solution

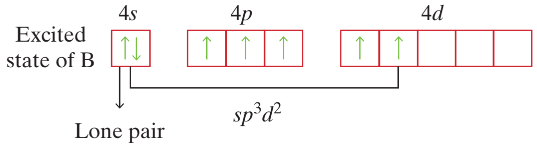
In PCl_5, the electronic configuration of P is [Ne] $3s^2\,3p^3$

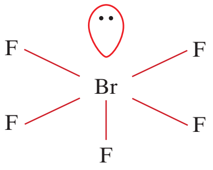




Trigonal bipyramidal

In BrF_5, the electronic configuration of Br is [Ar] $4s^2\,4p^5$



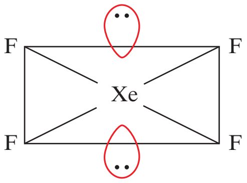


Square pyramidal

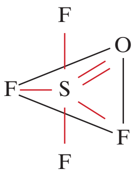
Solved Example 6-18

Draw the shape of XeF_4 and OSF_4 according to VSEPR theory. Show the lone pair of electrons on the central atom **(IIT-JEE 2004)**

Solution



Two lone pairs
Square planar
sp^3d^2



No lone pair
Trigonal bipyramidal
sp^3d

Solved Example 6-19

According to VSEPR theory, what is the most probable shape of the molecule having 4 electron pairs in the outermost shell of the central atom?

Solution

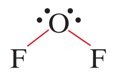
Tetrahedral shape is formed with the molecule having four electron pairs in the outermost shell of the central atom.

Solved Example 6-20

Using the VSEPR theory, identify the type of hybridization and draw the structure of OF_2. What are the oxidation states of O and F.

Solution

The structure of OF_2 is similar to H_2O and involves sp^3 hybridization on O atom having V-shape.



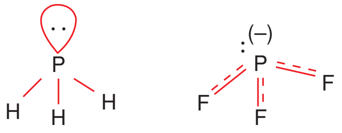
Oxidation number of oxygen = +2 and that of fluorine = –1

Note: Atoms tend to position themselves so that the maximum amount of orbital overlap occurs so that this yields the minimum potential energy, and therefore the strongest bonds.

6.9 | BACK BONDING

In some cases, there is a transfer of lone pair from a filled shell to an unfilled shell of an adjacent bonded atom. This transfer of electrons is a kind of π- bonding which may involve partial or complete transfer of electrons. Usually, the donor atoms that contain lone pair are F, O, N, C, Cl, Br, I, P, S, etc. Let us consider the following cases based on the nature of the donor atoms.

Case 1: Back bonding when fluorine is the donor atom.
Observation: The bond angle in PH_3 = 93.8° but the bond angle in PF_3 = 97.8°.
Explanation: Consider the following structures for the given molecules.

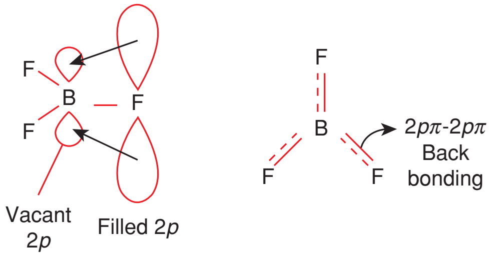


(a) (b)

In structure (a), according to Drago's rule, the bond angle should be around 90°. In structure (b), back bonding occurs between filled 2*p* orbitals of F and vacant orbitals 3*d* of P. As a result, though it is expected that due to higher electronegativity of F, the bond angle in PF_3 should be less, it is actually greater than H–P–H bond angle due to partial double bond character in P–F bond. Thus back bonding leads to decrease in P–F bond length and an increase in F–P–F bond angle.

Similarly the lower bond angle in case of AsH_3 (91.8°) < AsF_3 (96.2°) can be explained on the basis of back bonding.

Observation: The B–F bond length in BF_3 to shorter than expected.
Explanation: Consider the following structures for BF_3.

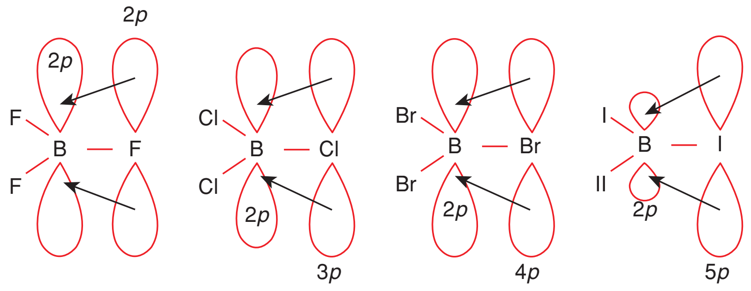


In BF_3, the back bonding occurs between filled 2*p* orbitals of F and vacant 2*p* orbitals of B. As a result, B–F bond length in BF_3 is shorter than expected.

Observation: The Lewis acidity order is as follows

$$BF_3 < BCl_3 < BBr_3 < BI_3$$

Explanation: For the explanation of the above observation, consider the following structures.



(a) (b) (c) (d)

The most effective back bonding is between filled $2p$ orbitals of F and vacant $2p$ orbitals of B. As the size of halide ion increases the effectiveness of overlap decreases. Therefore, the extent of back bonding is

$$(a) > (b) > (c) > (d)$$

Boron is electron deficient in all the cases. It is the most electron deficient when the extent of back bonding is the least. Therefore, the order of electron deficiency of boron atom is

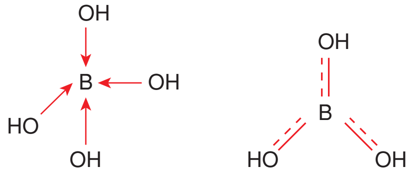
$$(a) < (b) < (c) < (d)$$

Thus, the Lewis acid strength is (a) < (b) < (c) < (d) or $BF_3 < BCl_3 < BBr_3 < BI_3$

Case 2: Back bonding when oxygen is the donor atom

Observation: The B–O bond length in $B(OH)_3$ is smaller than B–O bond length in $[B(OH)_4]^-$.

Explanation: Consider the following structures for the given molecules.



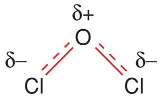
(a) (b)

In structure (a) for $[B(OH)_4]^-$, there is no back bonding in (a). In structure (b) for $B(OH)_3$, back bonding occurs between filled $2p$ orbitals of O and vacant $2p$ orbitals of B. Thus, B-O bond length in $B(OH)_3$ is shorter.

Observation: The order of bond angles $Cl_2O > H_2O > F_2O$ is

(110°8′) (104°5′) (103°2′)

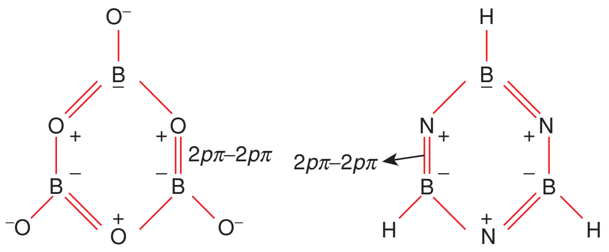
Explanation: In the given observation, the expected order of bond angles, based on electronegativity, is $H_2O > Cl_2O < F_2O$. However, the observed order of bond angles is $Cl_2O > H_2O > F_2O$



This deviation can be explained on the basis of back bonding that occurs between filled $2p$ orbitals of O and vacant $3d$ orbitals of Cl or $2p\pi - 3d\pi$ back bond formed.

Observation: Boroxine $[B_3O_6]^{3-}$ and borazine $[B_3N_3H_6]$ have planar structures.

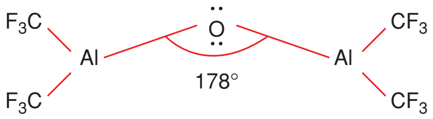
Explanation: Consider the following structures for the given compounds.



In both the cases full coordinate $2p\pi - 2p\pi$ back bonding occurs, resulting in a planar structure.

Observation: The $\angle Al-O-Al$ in $(F_3C)_2Al-O-Al(CF_3)_2$ is almost 180°.

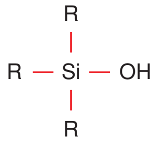
Explanation: Consider the following structure for $(F_3C)_2Al-O-Al(CF_3)_2$



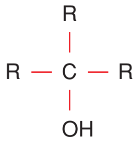
The back bonding occurs between filled 2*p* orbitals of O and vacant 3*d* orbitals of electron deficient Al. The extent of back bonding is enhanced due to the presence of electron withdrawing group CF_3 on Al. As a result, the hybridization is almost *sp* and bond angle approaches 180°.

Observation: R_3Si-OH is more acidic than R_3C-OH.

Explanation: Consider the following structures for the given compounds.

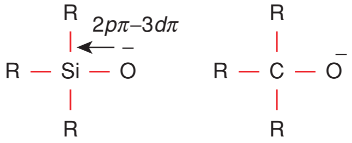


(a)



(b)

The conjugate bases are:

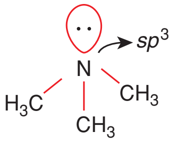


In structure (a) for $R_3Si–OH$, back bonding occurs which stabilizes the conjugate base of (a) due to $2p\pi - 3d\pi$ bond formation. However, no back bonding is possible in structure (b) for $R_3C–OH$.

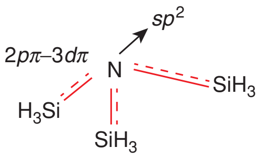
Case 3: Back bonding when nitrogen is the donor atom.

Observation: $(CH_3)_3N$ is pyramidal but $(SiH_3)_3N$ is planar.

Explanation: For the above observation, consider the following structures



(a)



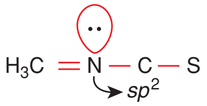
(b)

In structure (a), no back bonding occurs and thus the hybridization is sp^3 with one lone pair. As a result, the shape is pyramidal. In structure (b) $2p\pi - 3d\pi$ back bond is formed between filled 2*p* orbitals of N and vacant 3*d* orbitals of Si. As a result, the hybridization of N is now sp^2 and the shape is planar.

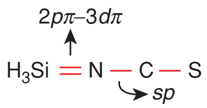
> **Note:** $P(SiH_3)_3$ is pyramidal and not planar like $NP(SiH_3)_3$. In $P(SiH_3)_2$, P has its own vacant *d* orbital and the inter- nuclear distance is large. Hence the tendency to donate lone pair is less and no back bonding takes place.

Observation: $H_3C - NCS$ is bent but $SiH_3 - NCS$ is linear.

Explanation: Consider the following structures given in the observations



(a)



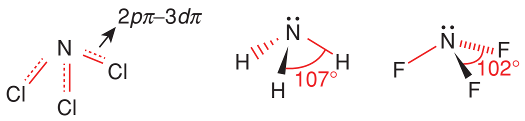
(b)

In structure (a), no back bonding is possible. In structure (b), back bonding occurs between filled 2*p* of N and vacant 3*d* of Si. As a result SiH_3-NCS is linear due to effective *sp* hybridization.

Observation: Order of bond angle: $NCl_3 > NH_3 > NF_3$ is

(107°45′) (107°) (102°)

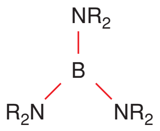
Explanation: Consider the following structures



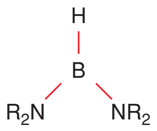
Back bonding occurs in NCl_3 between filled 2*p* orbitals of N and vacant 3*d* orbitals of Cl. As a result, hybridization approaches sp^2 and bond angle increase.

Observation: The order of bond length of B–N: $B(NR_2)_3 > HB(NR_2)_2 > H_2B–NR_2$

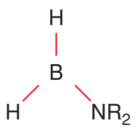
Explanation: Consider the following structures for the given compounds.



(a)



(b)



(c)

Due to steric crowding, the back bonding is most restricted in (a) and most feasible in (c). Therefore, the extent of back bonding is (a) < (b) < (c) and order of B–N bond length is (a) > (b) > (c).

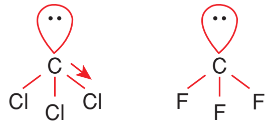
Case 4: Back bonding when carbon is the donor atom.

Observation: $CHCl_3$ is more acidic than CHF_3.

Explanation: This is explained as follows

$$CHCl_3 \rightleftharpoons H^+ + \bar{C}Cl_3$$

$$CHF_3 \rightleftharpoons H^+ + \bar{C}F_3$$



Observation: The relative stability order of diradicals is $:CH_2 <:CCl_2 <:CF_2$

Explanation: In $:CH_2$, the carbon atom is electron deficient due to incomplete octet and no back bonding, while in $:CF_2$ and $:CCl_2$ $2p\pi-2p\pi$ and $2p\pi-3p\pi$ back donation takes place, respectively. The $2p\pi-2p\pi$ bonding is more effective than $2p\pi-3p\pi$ back donation. So, $:CF_2$ is more stable as compared to $:CCl_2$.

Observation: R_3C^- is pyramidal while $(CN)_3C^-$ is planar.

Explanation: This can be explained on the basis of back bonding from the lone pair of carbon atom into the π^* orbital of the CN group.

Note: In all of the following: P = O, Cl = O, S = O, π bonds are $p\pi-d\pi$ bonds between filled *p* orbitals of O and vacant *d* orbitals of P, Cl, S.

The relative strength of bonds are in the order:

$2p\pi - 2p\pi > 2p\pi - 3d\pi > 2p\pi - 3p\pi > 3p\pi - 3p\pi$

($2p\pi - 3d\pi$ is stronger due to inclined nature of 3*d* orbital.)

Bridge Bonding

A bridge bond is a type of bond which forms in some hydrogen compounds such as B_2H_6 and BeH_2. Let us consider the following examples of bridge bonding.

1. **Diborane (B_2H_6):** It is observed that BH_3 molecules do not exist in monomeric form at ordinary conditions, and undergo dimerization readily as shown in Fig. 6.16.

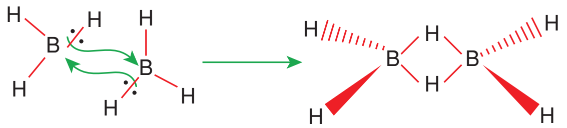


Figure 6.16 Dimerization of BH_3 molecule.

$$2BH_3 \rightleftharpoons B_2H_6$$

B_2H_6 exists as $[BH_4]^+ [BH_2]^- \rightleftharpoons [BH_4]^- [BH_2]^+$

In this case one bond pair of B–H is shared with the other B to fulfill the octet rule. As a result two electrons are shared between three atom (B, H, B) and it is known as 2 electron–3 center (2e – 3c) bond. The hybridization of both boron atoms is sp^3. The electronic distribution of the bridge bond (B-H-B) has a banana like appearance and is also called **banana bond**.

The B–H bond length in terminal bonds is less than the B–H bond length in the bridge bonds. Also, more energy is required to remove the hydrogen atom from the bridged position than the terminal position. This is because the bridged overlap is of σ type and is considered $sp^3 - s - sp^3$ overlap.

2. **BeH_2:** In beryllium hydride, Be is *sp* hybridized and the shape is linear. The existence of the dimer Be_2H_4 and higher polymeric forms $(BeH_2)_n$ can also be explained on the basis of bridge bonding as shown in Fig. 6.17.

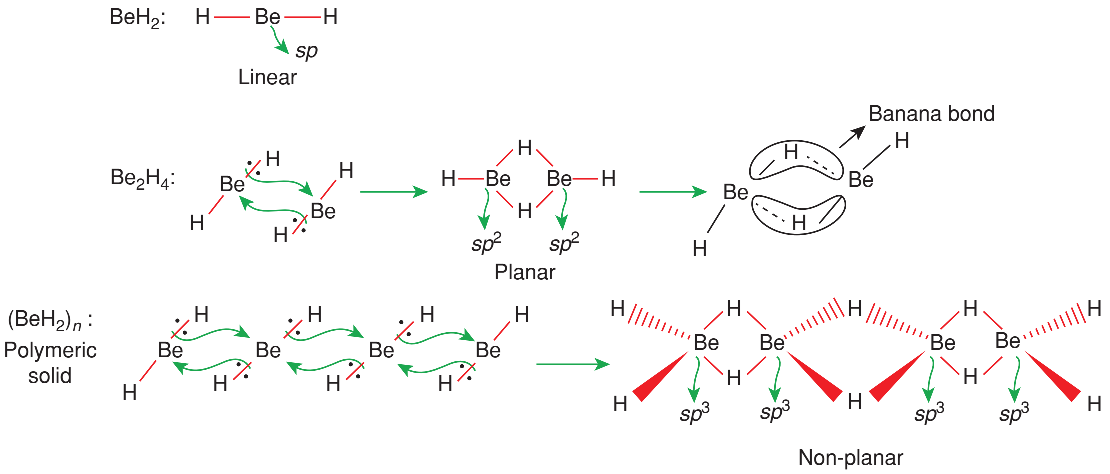


Figure 6.17 Bonding in BeH_2 and bridge bonding in Be_2H_4 and $(BeH_2)_n$.

3. **Beryllium chloride ($BeCl_2$):** In $BeCl_2$, Be is *sp* hybridized and structure is linear. In Be_2Cl_6 and $(BeCl_2)_n$ the bridge bond in Be–Cl–Be is (4e–3c) bond (Fig 6.18).

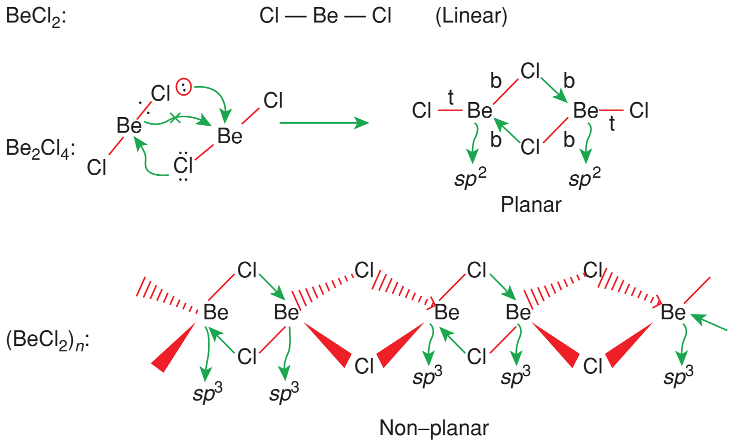


Figure 6.18 Bonding in $BeCl_2$ and bridge bonding in Be_2Cl_4 and $(BeCl_2)_n$.

4. **I_2Cl_6:** The bridge bonding in ICl_3 leads to formation of dimeric compound.

$$2ICl_3 \rightleftharpoons I_2Cl_6$$

Both iodine atoms are sp^3d^2 hybridized and the molecule is planar to minimize repulsion, as shown in Fig. 6.19

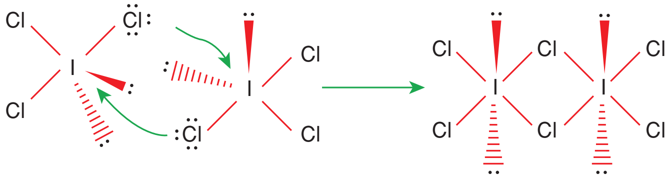


Figure 6.19 Structure of I_2Cl_6.

Some molecules showing bridge are listed in Table 6.8 along with nature of bond and planarity.

Table 6.8 Molecules showing bridge bonding

Molecules	Nature of bonds (3c–2e/3c–4e)	Planar (P) and Non-planar (NP)
Al_2Cl_6	3c–4e	NP
Al_2Br_6	3c–4e	NP
$(AlH_3)_8$	3c–2e	NP
Al_2I_6	3c–4e	NP
$Al_2(CH_3)_6$	3c–2e	NP
I_2Cl_6	3c–4e	P

6.10 | IONIC BONDING

Ionic solids are held together by the electrostatic attraction between the positive and negative ions. The attractive force will be a maximum when each ion is surrounded by the greatest possible number of oppositely charged ions. The formation of an ionic compound and its stability primarily depend on:

1. The ease of formation of ions.
2. The arrangement of positive and negative ions in the ionic solid or the lattice structure of the crystal.

Formation of Ionic Bond

The formation of an ionic compound will depend upon:

1. **Ionization enthalpy:** It is the enthalpy change that accompanies the removal of an electron from the outermost shell of an isolated gaseous atom to form a positive ion in gas phase. Lesser the ionization enthalpy, greater will be the energy released on formation of a positive ion and greater will be the ease of formation of an ionic bond.
2. **Electron gain enthalpy:** It is the enthalpy change that accompanies the addition of an extra electron to a gaseous isolated atom to form a negative ion in gas phase. Higher the electron gain enthalpy, greater will be the energy released on formation of a negative ion and greater will be the ease of formation of an ionic bond.
3. **Lattice enthalpy:** It is defined as the change in energy that occurs when isolated ions in the gas phase combine to form one mole of ionic compound. It is determined by the size of the ions and the charge on them. Greater the value of lattice enthalpy of the resulting ionic compound, greater will be the ease of its formation and its stability.

Metals, at the left of the periodic table, are elements with small ionization enthalpies and electron gain enthalpies. Relatively little energy is needed to remove electrons from them to produce positive ions. They tend to form positive ions. Non-metals, at the upper right of the periodic table, have large ionization enthalpies and generally exothermic electron gain enthalpies. It is quite difficult to remove electrons from these elements, but sizable amounts of energy are released when they gain electrons. They tend to form negative ions.

For ionic bonding to occur, the energy-lowering effect of the lattice enthalpy must be greater than the combined net energy-raising effects of the ionization enthalpy and electron gain enthalpy. On an energy basis, therefore, it is least "expensive" to form a cation from a metal and an anion from a non-metal. so it is relatively easy for the energy-lowering effect of the lattice enthalpy to exceed the net energy-raising effect of the ionization enthalpy and electron gain enthalpy. In fact, metals combine with non-metals to form ionic compounds simply because ionic bonding is favored energetically over other types whenever atoms with small ionization enthalpies combine with atoms that have large exothermic electron gain enthalpies.

The magnitude of the electrostatic or coulombic attraction between the particles depends on the product of the charges (q_1 and q_2) on the two ions and the square of the distance between the ions (r^2).

$$F = \frac{q_1 \times q_2}{r^2}$$

Let us consider formation of sodium chloride from its elements that involves formation of the sodium and chloride ions. The formation of this ions is related to the potential energy of the system of reactants and products. This is because *for any stable compound to form from its elements, there must be a net lowering of the potential energy* or the reaction must be exothermic.

Note: Keep in mind the relationship between potential energy changes and endothermic and exothermic processes:

Endothermic process ⇒ Increase in potential energy
Exothermic process ⇒ Decrease in potential energy

In case of gaseous atoms, we need to consider the ionization enthalpy and electron gain enthalpy of sodium and chlorine, respectively.

Ionization enthalpy of sodium: $\text{Na} \rightarrow \text{Na}^+ + e^- \quad (+495.4 \text{ kJ mol}^{-1})$
Electron gain enthalpy for chlorine: $\text{Cl} + e^- \rightarrow \text{Cl}^- \quad (-348.8 \text{ kJ mol}^{-1})$

The sum of the energy changes associated with the formation of both the ions is + 146.6 kJ mol^{-1}. This shows that the formation of ions from gaseous sodium and chlorine require a substantial increase in the potential energy. The driving force for the formation of the compound, and its stability can be explained by the **lattice enthalpy**.

In the above energy considerations, we have considered the gaseous state of sodium and chloride atoms. However, the compound NaCl is a solid in which the ions are packed together in a way that maximizes the attractions between oppositely charged ions. If we were to pull apart the ions to form gaseous ions, the process would require a lot of work and would lead to a large increase in the potential energies of the ions. The **lattice enthalpy** *is the energy required to completely separate the ions in one mole of a solid compound from each other to form gaseous ions.* For sodium chloride, the process associated with the lattice enthalpy and in equation form can be represented as

$$\text{NaCl(s)} \rightarrow \text{Na}^+\text{(g)} + \text{Cl}^-\text{(g)}$$

The energy associated with this change (the *lattice enthalpy* of sodium chloride) has been both measured and calculated to be +787.0 kJ mol^{-1}. The positive sign means that it takes 787.0 kJ to separate the ions of one mole of NaCl. It also means that if we bring together a mole of Na^+ and Cl^- ions from the gaseous state into one mole of crystalline NaCl, 787 kJ will be released. If we now include the lattice enthalpy (with its sign reversed because we are changing the direction of the change) along with the ionization enthalpy and electron gain enthalpy we have

$$\begin{array}{ll} \text{Na(g)} \rightarrow \text{Na}^+\text{(g)} + e^- & +495.4 \text{ kJ (Ionization enthalpy of Na)} \\ \text{Cl(g)} + e^- \rightarrow \text{Cl}^-\text{(g)} & -348.8 \text{ kJ (Electron gain enthalpy of Cl)} \\ \text{Na}^+\text{(g)} + \text{Cl}^-\text{(g)} \rightarrow \text{NaCl(s)} & -787.0 \text{ kJ (–Lattice energy)} \\ \hline \text{Net reaction: Na(g) + Cl(g)} \rightarrow \text{NaCl(s)} & -640.4 \text{ kJ} \end{array}$$

Thus, the release of energy equivalent to the lattice enthalpy provides a large net lowering of the potential energy as solid NaCl is formed. In other words, we can say that it is the lattice enthalpy that provides the stabilization necessary for the formation of NaCl. Lattice enthalpies are endothermic and so are given positive signs. For any ionic compound, the chief stabilizing influence is the lattice enthalpy, which when released is large enough to overcome the net energy input required to form the ions from the elements.

Lattice Enthalpy

For an ionic compound to be formed from its elements, the exothermic release of the lattice enthalpy must be larger than the endothermic combination of factors involved in the formation of the ions themselves, which primarily involve the ionization enthalpy of the metal and the electron enthalpy of the non-metal.

Lattice enthalpy for ionic compounds can be calculated theoretically from **Born Lande's** equation as

$$\Delta_{\text{lattice}} H = -\frac{N_A Z^+ Z^- e^2 A}{4\pi\varepsilon_0 r_0}\left(1-\frac{1}{n}\right) \tag{6.2}$$

where N_A = Avogadro constant; A = Madelung constant, relating to the geometry of the crystal; Z^+ = charge number of cation; Z^- = charge number of anion; e = charge of electron 1.6022×10^{-19} C and $\in_0$ = permittivity of free space; r_0 = distance to closest ion; n = Born exponent, typically a number between 5 and 12. The Born exponent is determined experimentally by measuring the compressibility of the solid, or derived theoretically.

Substituting $4\pi\in_0 = 1.112 \times 10^{-10}$ C^2 J^{-1}·m^{-1}, $N_A = 6.023 \times 10^{23}$ and $e = 1.6022 \times 10^{-19}$ C, we get

$$\Delta_{\text{lattice}} H = 1.39 \times 10^5 \left(\frac{Z^+ Z^- A}{r_0}\right)\left(1-\frac{1}{n}\right) \tag{6.3}$$

Note: Another term called **hydration enthalpy** is the energy released when the ions of an ionic compound are attached to water molecules.

The lattice enthalpies of some ionic compounds are given in Table 6.9. Their magnitudes depend on a number of factors, including the sizes of the ions and their charges. In general, as the ions become smaller, the lattice enthalpy increases; smaller ions allow the charges to get closer together which makes them more difficult to pull apart. For example, the lattice enthalpy for LiCl is larger than that for NaCl.

Table 6.9 Lattice enthalpies of some ionic compounds

Compound	Ions	Lattice enthalpy (kJ mol^{-1})
LiCl	Li^+ and Cl^-	845
NaCl	Na^+ and Cl^-	787
KCl	K^+ and Cl^-	709
LiF	Li^+ and F^-	1033
$CaCl_2$	Ca^{2+} and Cl^-	2258
$AlCl_3$	Al^{3+} and Cl^-	5492
CaO	Ca^{2+} and O^{2-}	3401
Al_2O_3	Al^{3+} and O^{2-}	15,916

The lattice enthalpy also becomes larger as the amount of charge on the ions increases, because more highly charged ions attract each other more strongly. Thus, salts of Ca^{2+} have larger lattice energies than comparable salts of Na^+, and those containing Al^{3+} have even larger lattice energies. Besides affecting the ability of ionic compounds to form, lattice energies are also important in determining the solubilities of ionic compounds in water and other solvent.

Lattice enthalpies cannot be measured directly, but experimental values are obtained from thermodynamic data using the Born–Haber cycle.

Born–Haber Cycle

We cannot measure the lattice enthalpy for sodium chloride directly, but we can use Hess' law and some other experimental data to calculate the lattice enthalpy indirectly. We have learnt that the enthalpy change for a process is the same regardless of the path we follow from start to finish. With this in mind, we can construct a set of alternate paths from the free elements to the solid ionic compound. This is called a **Born–Haber cycle** after the scientists who were the first to use it to calculate lattice energies, and is shown in Fig. 6.20 for the formation of sodium chloride.

We begin with the free elements, sodium and chlorine. The direct path at the bottom left has as its enthalpy change the heat of formation of NaCl, $\Delta_f H^\circ$.

$$\text{Na(s)} + \tfrac{1}{2}\text{Cl}_2\text{(g)} \rightarrow \text{NaCl(s)}; \quad \Delta_f H^\circ = -411.3 \text{ kJ}$$

The alternative path is divided into a number of steps. The first two steps, both of which have ΔH° values that can be measured experimentally, are endothermic. They change Na(s) and Cl_2(g) into gaseous atoms, Na(g) and Cl(g). The next two steps change these atoms to ions, first by the endothermic ionization enthalpy of Na followed by the exothermic electron gain enthalpy of Cl. This brings us to the gaseous ions, Na^+(g) and Cl^-(g). Notice that at this point, if we add all the energy changes, the ions are at a considerably higher energy than the reactants. If these were the only energy terms involved in the formation of NaCl, the heat of formation would be endothermic and the compound would be unstable; it could not be formed by direct combination of the elements.

The last step on the right finally brings us to solid NaCl and corresponds to the negative of the lattice enthalpy. (Remember, the lattice enthalpy is defined as the energy needed to *separate* the ions; in the last step, we are *bringing the ions together* to form the solid.) To make the net energy changes the same along both paths, the energy released when the ions condense to form the solid must equal –787.0 kJ. Therefore, the calculated lattice enthalpy of NaCl must be +787.0 kJ mol^{-1}.

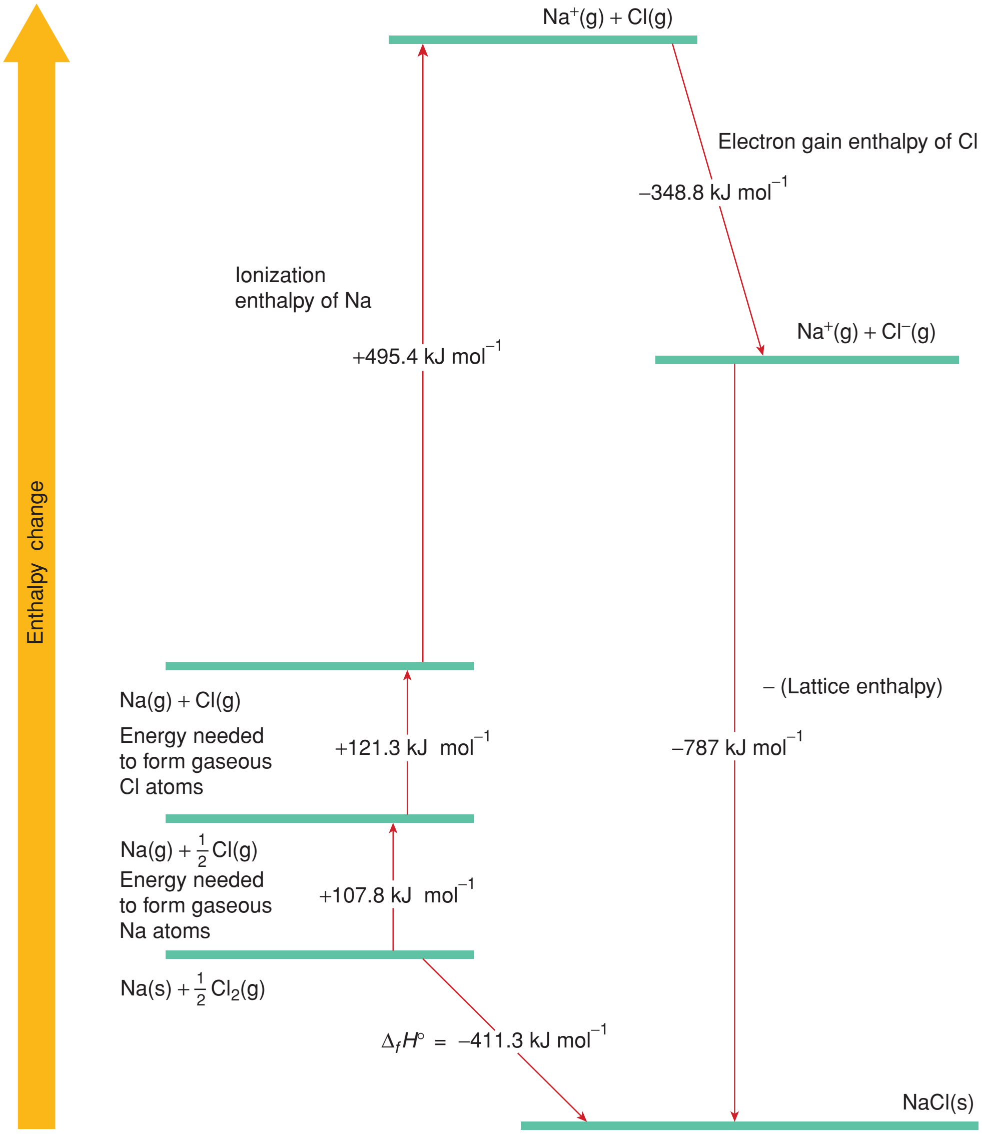


Figure 6.20 Born–Haber cycle for sodium chloride.

The path at the lower left labeled $\Delta_f H^\circ$ leads directly to NaCl(s). The upper path involves the formation of gaseous atoms from the elements, then the formation of gaseous ions from the atoms, and finally the condensation of Na^+ and Cl^- ions to give solid NaCl. The final step releases energy equivalent to the lattice enthalpy. The enthalpy changes accompanying each step can be listed as:

1. Sublimation of sodium metal

$$\mathrm{Na(s)} \to \mathrm{Na(g)}; \quad \Delta_{\mathrm{sub}} H^\circ = 107.8\ \mathrm{kJ\ mol^{-1}}$$

2. Ionization of sodium atoms

$$\mathrm{Na(g)} \to \mathrm{Na^+(g)} + e^-; \quad \Delta_{\mathrm{ion}} H^\circ = 495.4\ \mathrm{kJ\ mol^{-1}}$$

3. Dissociation of chlorine into atoms

$$\tfrac{1}{2}\mathrm{Cl_2(g)} \to \mathrm{Cl(g)}; \quad \tfrac{1}{2}\Delta_{\mathrm{bond}} H^\circ = 121.3\ \mathrm{kJ\ mol^{-1}}$$

4. Gain of electron by chlorine

$$\mathrm{Cl(g)} + e^- \to \mathrm{Cl^-(g)}; \quad \Delta_{\mathrm{EA}} H^\circ = -348.8\ \mathrm{kJ\ mol^{-1}}$$

5. The lattice enthalpy

$$\mathrm{Na^+(g)} + \mathrm{Cl^-(g)} \to \mathrm{Na^+Cl^-(s)}$$
$$\Delta_{\mathrm{lattice}} H^\circ = 411.3 + 107.8 + 121.3 + 495.4 - 348.8\ \mathrm{kJ\ mol^{-1}} = 787.0\ \mathrm{kJ\ mol^{-1}}$$

The applications of Born–Haber cycle are:

1. It is used to calculate of lattice enthalpies, electron gain enthalpies and ionization enthalpies of ionic compounds.
2. It helps in understanding the thermodynamic stability of molecules.

Properties of Ionic Compounds

The compounds resulting from the non-directional ionic bond, namely, ionic compounds are characterized by the following properties:

1. All ionic compounds adopt a three-dimensional structure in which the ions are close to various oppositely charged ions, that is, they are highly crystalline solids.
2. They are thermally stable and have high density, high melting and boiling points due to stronger electrostatic force of attraction between oppositely charged ions.
3. They are hard and brittle.
4. Being highly polar, they are soluble in polar solvents.
5. They have low electrical conductivity as solids but are good conductors in molten state or in aqueous solution due to availability of free ions.

Solved Example 6-21

Calculate the lattice enthalpy of calcium oxide from the following data: $\Delta_{\mathrm{atom}} H^\circ(\mathrm{Ca}) = 178\ \mathrm{kJ\ mol^{-1}}$; $\Delta_{\mathrm{IE_1}} H = 590\ \mathrm{kJ\ mol^{-1}}$; $\Delta_{\mathrm{IE_2}} H = 1150\ \mathrm{kJ\ mol^{-1}}$; $\Delta_{\mathrm{atom}} H(\mathrm{O_2}) = 249\ \mathrm{kJ\ mol^{-1}}$; $\Delta_{\mathrm{EA_1}} H^\circ(\mathrm{O}) = -141\ \mathrm{kJ\ mol^{-1}}$; $\Delta_{\mathrm{EA_2}} H^\circ(\mathrm{O}) = 844\ \mathrm{kJ\ mol^{-1}}$; $\Delta_f H^\circ(\mathrm{CaO}) = -635\ \mathrm{kJ\ mol^{-1}}$.

Solution

From the Born–Haber cycle, we have

$$\Delta_f H^\circ + \Delta_{\mathrm{lattice}} H^\circ = \Delta_{\mathrm{atom}} H^\circ(\mathrm{Ca}) + (\Sigma\Delta_{\mathrm{IE}} H^\circ) + \Delta_{\mathrm{atom}} H^\circ(\mathrm{O}) + (\Sigma\Delta_{\mathrm{EA}} H^\circ)$$

Substituting values, we get

$$\begin{aligned}\Delta_{\mathrm{lattice}} H^\circ &= \Delta_{\mathrm{atom}} H^\circ(\mathrm{Ca}) + (\Sigma\Delta_{\mathrm{IE}} H^\circ) + \Delta_{\mathrm{atom}} H^\circ(\mathrm{O}) \\ &\quad + (\Sigma\Delta_{\mathrm{EA}} H^\circ) - \Delta_f H^\circ \\ &= 178 + (590 + 1150) + 249 + (-141) + 844 - (-635) \\ &= 3505\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

Solved Example 6-22

Consider an ionic compound MX_2 where M is a metal that forms a cation of +2 charge, and X is a non-metal that forms an anion of –1 charge. A Born–Haber cycle for MX_2 is shown in Fig. 6.21. Each step in this cycle has been assigned a number (A – G).

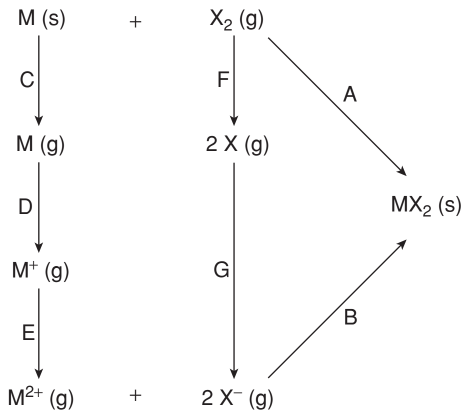


Figure 6.21

(a) Identify the steps that are endothermic.

(b) Which step corresponds to $\Delta_{sub}H^o$?

(c) Which step corresponds to $\Delta_f H^o$?

(d) Use the following energy values to calculate the lattice enthalpy (in kJ mol^{-1}) for MX_2. $\Delta_{sub}H^o = 296$ kJ mol^{-1}; $\Delta_f H^o = -421$ kJ mol^{-1}; $\Delta_{IE_1}H = 378$ kJ mol^{-1}; $\Delta_{IE_2}H = 555$ kJ mol^{-1}; $\Delta_{diss}H^o = 310$ kJ mol^{-1}; $\Delta_{EA}H^o = -427$ kJ mol^{-1}.

Solution

(a) Steps C, D, E and F are endothermic.

(b) Step C corresponds to $\Delta_{sub}H^o$.

(c) Step A corresponds to ΔH_f^o.

(d) From the Born–Haber cycle, we have

$$\Delta_f H^o = \Delta_{sub}H^o + \Delta_{IE_1}H^o + \Delta_{IE_2}H^o + \Delta_{diss}H^o + 2(\Delta_{EA}H^o) - \Delta_{lattice}H^o$$

$$-421 = 296 + 378 + 555 + 310 + 2(-427) - (-421) - \Delta_{lattice}H^o$$

Solving, we get $\Delta_{lattice}H^o = 1106$ kJ mol^{-1}

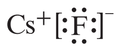
Concept of Electronegativity and Fajans' Rules

The degree to which a covalent bond is polar depends on the difference in the abilities of the bonded atoms to attract electrons. The greater the difference, the more polar the bond, and the more the electron density is shifted toward the atom that attracts electrons more. The term that we use to describe the attraction an atom has for the electrons in a bond is called **electronegativity**.

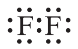
In 1931, Pauling defined the electronegativity of an atom as the tendency of the atom to attract the shared pair of electrons to itself *when combined in a compound*. The implication of this is that when a covalent bond is formed, the electrons used for bonding need not be shared equally by both atoms. When two identical atoms form a covalent bond, as in H_2 or Cl_2, each atom has an equal share of the bonding electron pair. The electron density at both ends of the bond is the same, because the electrons are equally attracted to both nuclei. If electrons are shared equally, the bond is known as a **non-polar bond**.

However, when different kinds of atoms combine, as in HCl, one nucleus usually attracts the electrons in the bond more strongly than the other. The result of unequal attractions for the bonding electrons is an unbalanced distribution of electron density within the bond, thus causing the one atom to have slightly postive charge and the other to have slightly negative charge. These charges are less than full 1+ and 1– charges and are called **partial charges**, which are usually indicated by the lowercase Greek letter delta, δ. Partial charges can also be indicated on Lewis structures. This is known as polarization of a covalent bond. For example, consider HCl molecule

In the extreme case where the bonding electrons are around one atom all the time, the bond is ionic. Pauling and others have attempted to relate the electronegativity difference between two atoms to the amount of ionic character in the bond between them. If two atoms have similar electronegativities, that is, a similar tendency to attract electrons, the bond formed between them will be predominantly covalent. Conversely, a large difference in electronegativity leads to formation of a bond with a high degree of **polar character**, that is, a predominantly ionic bond.



Bonding pair held exclusively by flourine



Bonding pair shared equally

Note: It is important to note that electronegativity is distinct from electron gain enthalpy. The former is a tendency of an atom to attract a shared pair of electrons in a molecule, whereas the latter is a property of an isolated atom and is measure of tendency of an atom to gain an electron.

Measurement of Electronegativity Values

1. **Pauling's scale:** Pauling pointed out that since reactions of the type:

$$A_2 + B_2 \rightarrow 2AB$$

are almost always exothermic, the bond formed between the two atoms A and B must be stronger than the average of the single bond energies of A

$$\frac{(I+E)}{(2\times 2.8\times 96.48)} \text{ or } \frac{(I+E)}{540.3}$$

This method has a simple theoretical basis, and also has the advantage that different values can be obtained for different oxidation states of the same element. It suffers from the limitation that only a few electron gain enthalpies are known. It is more usual to use the approach based on bond energies.

Solved Example 6-23

Calculate the electronegativity of fluorine on Pauling and Muliken's scales, given that the bond energies of H

Applications of Fajans' Rule

1. The compound with higher covalent character will have a lower melting and boiling point. For example, $BeCl_2$ (m.p. = 450°C) and $CaCl_2$ (m.p. = 782°C).
2. Greater the covalent character, lower is its solubility in polar solvents. For example, AgF > AgCl > AgBr > AgI.
3. Greater the covalent character, thermal stability decreases. For example, $BeCO_3 < MgCO_3 < CaCO_3 < BaCO_3$.

Polarity of Bonds and Dipole Moment

By studying electronegativity values and their differences we find that there is no sharp dividing line between ionic and covalent bonding. Ionic bonding and *non-polar covalent bonding* simply represent the two extremes. A bond is mostly ionic when the difference in electronegativity between two atoms is very large; the more electronegative atom acquires essentially complete control of the bonding electrons. The description of nature of bond between two species as completely ionic or covalent is an ideal case scenario. In reality, all bonds have some covalent or ionic character in them.

When two atoms compete for a pair of electrons in a bond, there are three possibilities for the pair of electrons, depending on difference in electronegativity of the two atoms:

1. If the difference in electronegativity is 1.8 or greater on the Pauling scale, it indicates that one atom has gained complete control of the pair of electrons and the bond is most likely ionic (e.g., NaCl).
2. Both atoms share the electrons equally (an electronegativity difference between the two atoms of zero or near zero), forming a non-polar bond (e.g., Cl_2).
3. The two atoms share electrons unequally (an electronegativity difference of less than 1.8), forming a polar bond. This is intermediate between purely ionic and equal sharing (e.g., HCl).
4. The noble gases are assigned electronegativities of zero (e.g., Ar).

There is a significant difference in electronegativity between H and Cl (0.9), indicating a polar bond, but not so much as to indicate an ionic bond. On the other hand, the difference in electronegativity between carbon (2.5) and hydrogen (2.1) is relatively small (0.4), so the bond is considered essentially non-polar.

Ionic Character in a Bond

The degree to which the bond is polar, which is the amount of **ionic character** of the bond, varies in a continuous way with changes in the electronegativity difference (Fig. 6.22). The bond becomes more than 50% ionic when the electronegativity difference exceeds approximately 1.7, which means that the atoms in the bond carry a partial charge of approximately ±0.5 units.

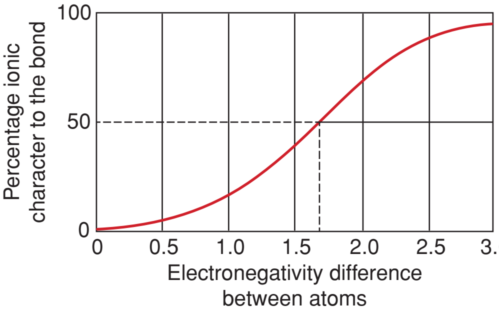


Figure 6.22 Variation in the percentage ionic character of a bond with electronegativity difference.

The percentage of polar character of a covalent bond can be calculated based on the difference in electronegativity of the two bonded atoms ($\chi_A - \chi_B$) using the two empirical relations:

1. Pauling equation which states percentage of ionic character $= 18(\chi_A - \chi_B)^{1.4}$
2. Hanney and Smith equation which states percentage of ionic character $= 16(\chi_B - \chi_A) + 3.5(\chi_B - \chi_A)^2$

Solved Example 6-25

Use Hanney and Smith equation to calculate the percentage ionic character in **(a)** H–F; **(b)** H–Cl and **(c)** Si–H. The electronegativities of H, F, Cl and Si are, respectively, 2, 3, 4 and 1.8.

Solution

(a) For H–F, the percentage ionic character

$$16(\chi_F - \chi_H) + 3.5(\chi_F - \chi_H)^2 = 16(3-2) + 3.5(3-2)^2$$
$$= 16 + 3.5 = 19.5\%$$

(b) For H–Cl, the percentage ionic character

$$16(\chi_{Cl} - \chi_H) + 3.5(\chi_{Cl} - \chi_H)^2 = 16(4-2) + 3.5(4-2)^2$$
$$= 32 + 14 = 46\%$$

(c) For Si–H, the percentage ionic character

$$16(\chi_H - \chi_{Si}) + 3.5(\chi_H - \chi_{Si})^2 = 16(2-1.8) + 3.5(2-1.8)^2$$
$$= 3.2 + 0.14 = 3.34\%$$

Solved Example 6-26

How does bond polarity affect the percentage of ionic character of the bond and the bond length? Explain. Determine the percentage of ionic character of H

$$\overset{+\delta}{\mathrm{H}}-\overset{-\delta}{\mathrm{Cl}} \qquad\qquad \overset{+\!\!\longrightarrow}{\mathrm{H}-\mathrm{Cl}}$$

Partial charges Dipole moment

For molecules that contain more than two atoms (polyatomic molecules), however, we have to consider the combined effects of all the bonds. Bond dipoles can be treated as vectors, and the polarity of a molecule is predicted by taking the vector sum of the bond dipoles. Sometimes, when all the atoms attached to the central atom are the same, the effects of the individual polar bonds cancel and the molecule as a whole is non-polar. Some examples are shown in Fig. 6.23.

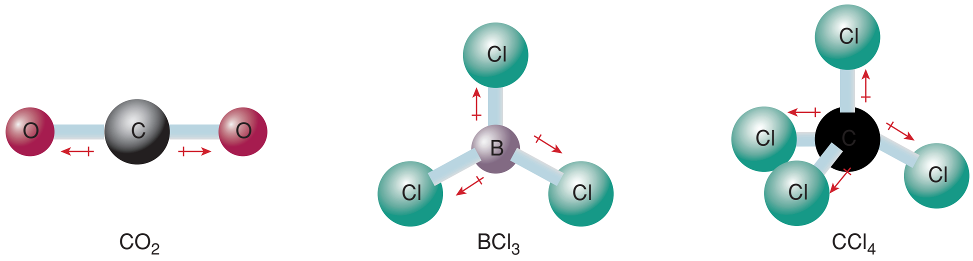


Figure 6.23 In symmetric molecules such as these, the bond dipoles cancel to give non-polar molecules.

The CO_2 molecule is symmetric. Both bonds are identical, so each bond dipole is of the same magnitude. Because CO_2 is a linear molecule, these bond dipoles point in opposite directions and work against each other. The net result is that their effects cancel, and CO_2 is non-polar. The same thing also happens in BCl_3 and CCl_4. In case of BF_3, the resultant dipole of two B

Note: Not every structure that contains lone pairs on the central atom produces polar molecules. The following are two exceptions (Fig. 6.26).

In the first case, we have a pair of bond dipoles arranged linearly, just as they are in CO_2. In the second, the bonded atoms lie at the corners of a square, which can be viewed as two linear sets of bond dipoles. *If the atoms attached to the central atom are the same*, cancellation of bond dipoles is bound to occur and produce non-polar molecules. This means that molecules such as linear XeF_2 and square planar XeF_4 are non-polar.

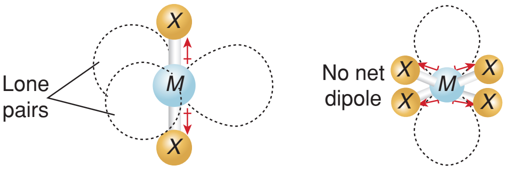
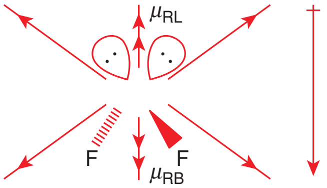


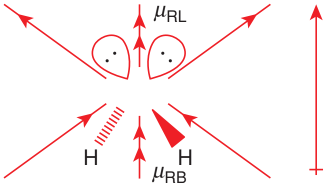
Figure 6.26 Exceptions having no dipole moment.

The contribution of the lone pair moment to the dipole moment of the molecule can be understood with the help of following examples.

Example 1: The dipole moment of F_2O is much lower than the dipole moment H_2O, though there is very small difference in electronegativity values of O–H and O–F bonds. In case of H_2O, the net dipole moment ($\mu_{H_2O} = \mu_{RB} + \mu_{RL}$) is much higher than the net dipole moment in F_2O ($\mu_{F_2O} = \mu_{RB} - \mu_{RL}$). Here μ_{RB} is the resultant vector of dipole moment of the bond pair and μ_{RL} is the resultant vector of dipole moment of lone pair.

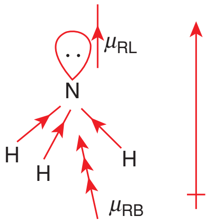


$\mu_{F_2O} = 0.3$ D

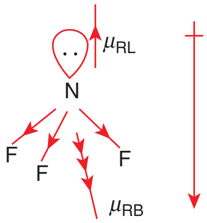


$\mu_{H_2O} = 1.84$ D

Example 2: The net dipole moment of NH_3 is much higher compared to that of NF_3, though there is very small difference in the electronegativity values of N–H and N–F bonds. In this case also the net dipole moment of NH_3 ($\mu_{NH_3} = \mu_{RB} + \mu_{RL}$) is much higher than the net dipole moment in NF_3 ($\mu_{NF_3} = \mu_{RB} - \mu_{RL}$).

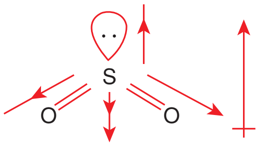


($\mu_{NH_3} = 1.5$ D)

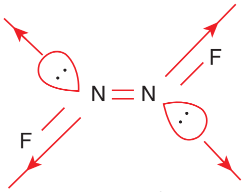


($\mu_{NF_3} = 0.2$ D)

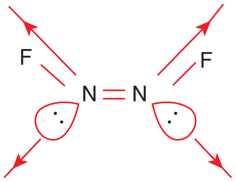
Example 3: The net dipole moment in case of SO_2 molecule is in the upward direction due to the presence of lone pair on sulphur.



Example 4: The net dipole moments of the *cis*-and *trans*-isomers of N_2F_2 are almost equal to zero due to the presence of lone pairs on each nitrogen atom.



$\mu_{\text{trans}} = 0$



$\mu_{\text{cis}} = 0.16$ D (approx 0 D)

Some special observations related to dipole moment are listed as follows:

Observation: The values of dipole moment of *o*-nitroaniline and *p*-nitroaniline are exceptionally high as compared to the expected values.

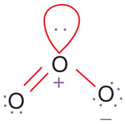
Explanation: This observation can be explained on the basis of $+R$ effect of $-NH_2$ group and $-R$ effect of $-NO_2$ coupled together that enhance the overall dipole moment values.

Observation: The dipole moment of Ph−F is less than that of Ph−Cl.

Explanation: This is due more effective mesomeric effect in case of F ($2p\pi - 2p\pi$ bonding) as compared to Cl ($3p\pi - 2p\pi$ bonding).

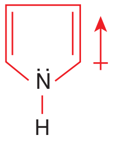
Observation: Ozone molecule is polar.

Explanation: O_3 is polar due to the dipole moment of the lone pairs as a result of which the resultant lone pair moment is not zero.

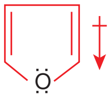


Observation: The net dipole moments of pyrrole and furan lie in the opposite directions.

Explanation: This can be explained on the basis of greater – I effect of O atom as compared to that of N atom. The mesomeric effect is almost the same as both show $2p\pi - 2p\pi$ bonding.



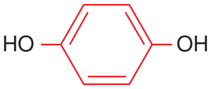
$\mu = 1.8$ D



$\mu = 0.7$ D.

Observation: Hydroquinone (1,4- benzenediol) shows net dipole moment of 1.64 D.

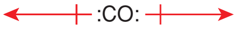
Explanation: 1,4-Benzenediol is expected to show zero dipole moment because of its symmetric structure. However, the net dipole moment is observed due to the presence of lone pair on oxygen atoms which are not involved in resonance with the benzene ring.



Observation: CO molecule has very low dipole moment of 0.112 D.

Explanation: The net dipole moment of CO is determined by the following contributing factors:

(i) The lone pair moments due to the presence on lone pairs on oxygen and carbon cancel each other.



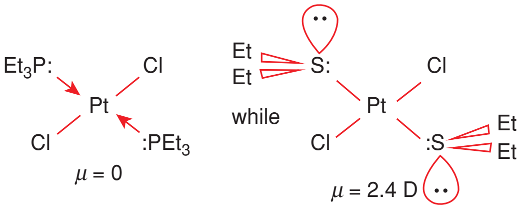
(ii) The resultant bond dipole moment in $:C=\ddot{\underset{\cdot\cdot}{O}}:$ is in the direction $\overset{+\!\!\!\longrightarrow}{\text{CO}}$.

(iii) The dative bond dipole moment in $:\overset{-}{C}\equiv\overset{+}{O}:$ opposes the bond dipole moment and reverses the direction from oxygen atom to carbon atom.

The net effect of the above factors is that the overall dipole moment is very less.

Observation: The dipole moment of $(Et_2S)_2PtCl_2$ is 2.4 D while $(Et_3P)_2PtCl_2$ has zero dipole moment.

Explanation: Consider the following structures for the given molecules.



The lone pairs on S atoms are not involved in dative bonding are oriented in a manner that their individual lone pair moments are not cancelled out.

Applications of Dipole Moment

1. **Determining the extent of polar character in a covalent bond:** Greater the magnitude of dipole moment, greater will be the polarity of the bond.
2. **Calculating the percentage ionic character of the bond:** This can be determined from the ratio of the expected dipole moment if the compound were 100% ionic ($\mu_{\text{ionic}} = \text{charge} \times \text{bond length}$) and the observed dipole moment (μ_{observed}).
3. **Predicting the shape of molecules and their symmetry:** In molecules containing three or more atoms with two or more polar bonds, if the dipole moment is zero, it implies that the shape of the molecule is not symmetrical. If the molecule contains similar atoms linked to the central atom with polar bonds and the net dipole moment is zero, it implies that the shape of the molecule is symmetrical.
4. **Distinguishing between *cis* and *trans* isomers:** The isomers can be identified as *cis* or *trans* based on the fact that *cis* isomers have higher dipole moment that *trans* isomers.
5. **Identifying the position of the substituent in substituted aromatic rings:** The substituent present in an aromatic ring can be identified to be at *ortho*, *meta* and *para* positions, based on the fact that dipole moment of *para* isomer is zero and that of *ortho* isomer is greater than that of *meta* isomer.

Solved Example 6-27

The HF molecule has a dipole moment of 1.83 D and a bond length of 91.7 pm. What is the amount of charge, in electronic charge units, on either end of the bond?

Solution

We use the expression $q = \frac{\mu}{r}$ to solve for q. The debye unit, D, equals 3.34×10^{-30} C m, so the dipole moment of HF is

$$\mu = 1.83 \times (3.34 \times 10^{-30}\ \text{C m}) = 6.11 \times 10^{-30}\ \text{C m}$$

The S.I. prefix p (pico) means $\times 10^{-12}$, so the bond length $r = 91.7 \times 10^{-12}$ m. Substituting in the equation above gives

$$q = \frac{6.11 \times 10^{-30}\ \text{C}\ \cancel{\text{m}}}{91.7 \times 10^{-12}\ \cancel{\text{m}}} = 6.66 \times 10^{-20}\ \text{C}$$

The amount of charge on an electron (i.e., an electronic charge unit) equals 1.602×10^{-19} C, which we can express as

$$1\ e = 1.602 \times 10^{-19}\ \text{C}$$

The value of q in electronic charge units is therefore

$$q = 6.66 \times 10^{-20} \left(\frac{1e}{1.602 \times 10^{-19}} \right) = 0.416e$$

As in HCl, the hydrogen carries the positive charge, so the charge on the hydrogen end of the molecule is $+0.416e$ and the charge on the fluorine end is $-0.416e$.

Solved Example 6-28

The dipole moment of KCl is 3.336×10^{-29} C m. The interatomic distance K^+ and Cl^- ion in KCl is 260 pm. Calculate the dipole moments of KCl, if there were opposite charges of the fundamental unit located at each nucleus. Calculate the percentage ionic character of KCl.

Solution

From the given data, and $q = 1.602 \times 10^{-19}\text{C}$

$$r = 260 \text{ pm} = 260 \times 10^{-12} \text{ m} = 2.6 \times 10^{-10} \text{ m}$$

Magnitude of dipole moment for 100% ionic character

$$|\mu| = qr = (1.602 \times 10^{-19})\,(2.6 \times 10^{-10}) = 4.165 \times 10^{-29} \text{ C m}$$

Actual dipole moment $= 3.336 \times 10^{-29}$ C m

$$\text{Therefore, \% of ionic bond} = \frac{3.336 \times 10^{-29}}{4.165 \times 10^{-29}} \times 100 = 80.1\%$$

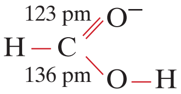
The bond is 80.1% ionic.

Solved Example 6-29

Methanoic acid, HCOOH, has one carbon-oxygen bond of length 123 pm, and another of 136 pm. Which bond has which length?

Solution

The structure of molecule is



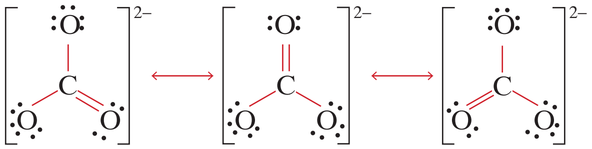
The double bonded carbon oxygen bond is shorter than the other. A double bond between two atoms is always stronger and shorter than a single bond between the same atoms and $HCOO^-$ have same bond length.

6.12 | RESONANCE STRUCTURES

Two equivalent Lewis structures can be written for sulphur dioxide, as shown in Fig. 6.27. The only difference between the two structures is the identity of the oxygen atom to which the double bond is formed. As a result, they must be equally satisfactory representations of the molecule. This raises an important question: Which of the Lewis structures for SO_2 is correct?

Interestingly, neither of the structures is correct. The two Lewis structures suggest that one of the sulphur–oxygen bond lengths is shorter than the other. Every experiment that is done to probe the structure of this molecule, however, suggests that the two sulphur–oxygen bonds have identical bond lengths. Moreover, the actual bond length is between that of an S meaning that all three bonds are identical and just as likely to contain the extra electrons. Experiments also tell us that the lengths of the three identical bonds are somewhere between those expected for a single and a double bond.

One Lewis representation of the CO_3^{2-} ion does not convey this information, but three resonance structures (connected by double-headed arrows) illustrate that all three bonds are just as likely to be a double bond. The actual structure of the molecule can be viewed as a resonance hybrid, or average, of the three structures.



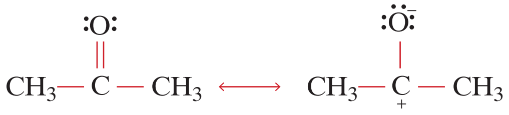
Note: It is important to distinguish between resonance structures and isomers, such as dimethyl ether and ethanol. Isomers have the same chemical formula but different arrangements of the atoms. Resonance structures have the same arrangement of atoms but a different arrangement of electrons, leading to multiple bonds in more than one position in the structures.

Some important points about resonance structures

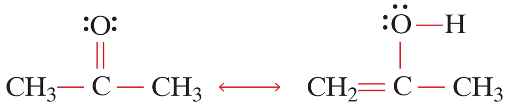
1. Resonance is exhibited only in molecules whose atoms are in one plane.
2. The resonance hybrid structure averages the bond characteristics of various resonance structures.
3. The canonical structures have no real existence but only help visualize the possible resonance structures.
4. There is no equilibrium between the canonical structures and the molecule does not exist as any of these structures at any interval of time.
5. All the canonical structures must have the same number of unpaired electrons.

Solved Example 6-30

Which sets are pairs of acceptable resonance contributing structures?

(a)


$$CH_3-\overset{\overset{:O:}{\|}}{C}-CH_3 \longleftrightarrow CH_3-\underset{+}{\overset{\overset{:\ddot{O}:^-}{|}}{C}}-CH_3$$

(b)


$$CH_3-\overset{\overset{:O:}{\|}}{C}-CH_3 \longleftrightarrow CH_2=\overset{\overset{:\ddot{O}-H}{|}}{C}-CH_3$$

Solution

(a) A pair of resonance contributing structures. They differ only in the distribution of valence electrons.

(b) Not a pair of resonance contributing structures. They differ in the arrangement of their atoms. Oxygen is bonded to a hydrogen atom in the Lewis structure on the right, but the other structure contains no such bond.

Solved Example 6-31

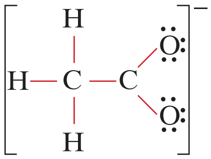
Acetic acid dissociates to some extent in water to give the acetate ion, CH_3COO^-. Write two alternative Lewis structures for the acetate ion.

Solution

We can start by noting that the acetate ion contains two carbon atoms (Group 14), three hydrogen atoms (Group 1), and two oxygen atoms (Group 16). It also carries a negative charge, which means that CH_3COO^- contains a total of 24 valence electrons.

$$CH_3COO^- \quad 2(4)+3(1)+2(6)+1=24$$

The skeleton structure contains six covalent bonds, which leaves 12 non-bonding electrons. Unfortunately, it takes all 12 non-bonding electrons to satisfy the octets of the oxygen atoms, which leaves no non-bonding electron for the carbon atom on the right in the following attempt at the Lewis structure of this molecule.



Because there are not enough electrons to satisfy the octets of the atoms, we assume that there is at least one C

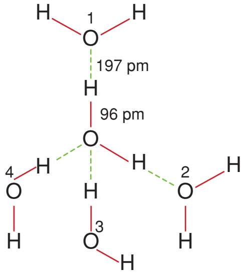


Figure 6.28 Hydrogen bonding in water molecule.

This results in electrostatic force of attraction that is represented as

$$\overset{\delta-}{N}—\overset{\delta+}{H}\text{----}\overset{\delta-}{N}—\overset{\delta+}{H}\text{----}\overset{\delta-}{N}—\overset{\delta+}{H}$$

The extent of hydrogen bonding depends on the physical state of the compound. It is the maximum in case of solids and minimum in the gaseous state. Hydrogen bonding can strongly influence the structure and properties of the compounds.

For example, the hydrogen atom in each water molecule is hydrogen bonded (dashed line) to the oxygen in four other water molecules as shown in Fig. 6.28.

A normal covalent bond length is 96 pm, while the hydrogen bond length is 197 pm. As the bond lengths indicate the bond strength, it can be seen that hydrogen bond is much weaker than the covalent and the ionic bonds. However, hydrogen bond energy is stronger than most other intermolecular forces and is in the range of 1–5 kcal mol^{-1}. This energy is smaller than covalent bond energy (~50–100 kcal mol^{-1}), but greater than thermal energy (0.6 kcal mol^{-1} at the room temperature).

In any species when hydrogen is bonded to a highly electronegative atom like F, O, N, then the bond is highly polar where H acquires a partial positive charge, while the electronegative atom acquires a partial negative charge, that is, $X^{\delta-} \rightarrow H^{\delta+}$.

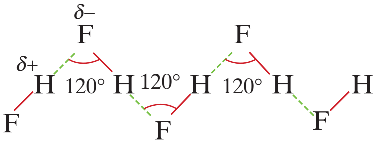
If a number of such species are brought nearer to each other, the positive end of one attracts the negative end of the other, developing a weak electrostatic attraction by hydrogen bonding.

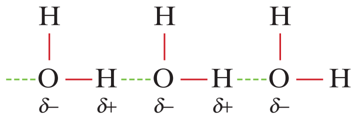
$$X\text{----}H^{\delta+}\text{----}X^{\delta-}\text{----}H^{\delta+}\text{----}X^{\delta-}\text{----}H$$

There are two types of hydrogen bonds, namely, intermolecular and intramolecular.

1. **Intermolecular hydrogen bond:** When the hydrogen bonding occurs between an H atom of one molecule and an electronegative atom of a second molecule, it is called intermolecular hydrogen bond. This type of intermolecular hydrogen bond exists between the molecules of hydrogen fluoride, alcohol, water, ammonia, etc.

   An intermolecular hydrogen bond results in the association of many molecules as a group. Effect of this intermolecular hydrogen bonding is reflected in many properties of the compounds such as increase in the melting point, boiling point, viscosity, surface tension, solubility, etc.

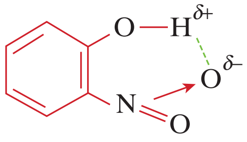




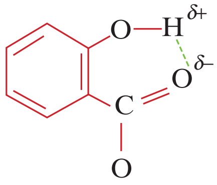
$$\text{----}\underset{\delta-}{\overset{\overset{H}{|}}{O}}—\underset{\delta+}{H}\text{----}\underset{\delta-}{\overset{\overset{H}{|}}{O}}—\underset{\delta+}{H}\text{----}\underset{\delta-}{\overset{\overset{H}{|}}{O}}—H$$

$$\underset{10\ \text{kcal mol}^{-1}}{H—F\text{----}H} > \underset{7\ \text{kcal mol}^{-1}}{H—O\text{----}H} > \underset{2\ \text{kcal mol}^{-1}}{H—F\text{----}H}$$

2. **Intramolecular hydrogen bond:** In this type, the hydrogen bond is formed between hydrogen and an electronegative atom (F, O, N), within the same molecule. An intramolecular hydrogen bond results in the chelation or ring formation of the molecules and prevents their association. Hence, this does not affect much the physical properties of the compounds. For example, intramolecular hydrogen bonds are present in molecules such as *o*-chlorophenol, salicylaldehyde, *o*-nitrobenzoic acid, etc.



o–Nitrophenol



o–Salicyclic acid

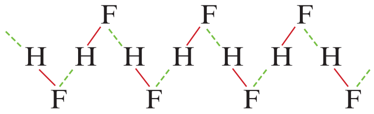
Consequences of Hydrogen Bonding

Hydrogen bonding has pronounced effects on many physical properties of compounds.

Physical State

Intermolecular hydrogen bonding causes two or more molecules of a compound to exist as associated or grouped molecules. This results in an increase in the size as well as the molecular mass of the compound which in turn is reflected in the physical state of the substance. For example, although both oxygen and sulphur belong to the same group, H_2O is a liquid at ordinary temperature, while H_2S is a gas. This is explained as follows:

In water, since oxygen (E.N. = 3.5) is highly electronegative, it forms intermolecular hydrogen bonds which results in many water molecules getting associated and hence result in an increase in the molecular mass. Consequently, water exists as liquid at room temperature. On the other hand, the difference in electronegativity of H (E.N. = 2.1) and S (E.N. = 2.5) atoms in H_2S is less and there is negligible hydrogen bonding in H_2S. Hence H_2S molecules are not associated and therefore H_2S exists as a gas at room temperature. By a similar reasoning, the existence of HF as a liquid and HCl as a gas can be explained.



Hydrogen fluoride

Melting and Boiling Points

The compounds containing hydrogen bonds have higher melting and boiling points. Due to intermolecular hydrogen bonding and a consequent association of molecules, larger energy is required to separate these molecules before they can melt or boil. Hence there is an elevation in the melting and boiling points of these compounds.

For example, the melting and boiling points of the hydrides of Group 14, namely, CH_4, SiH_4, GeH_4 and SnH_4 increase with increasing molecular weights. However, in the case of the hydrides of elements of Groups 15, 16 and 17, the melting and boiling points of H_2O, NH_3 and HF are exceptionally higher than the hydrides of other members of their groups due to the presence of intermolecular hydrogen bonding. This order of melting and boiling points is shown as follows:

Group 14: $CH_4 < SiH_4 < GeH_4 < SnH_4$

Group 15: $NH_3 > PH_3 < AsH_3 < SbH_3$

Group 16: $H_2O > H_2S < H_2Se < H_2Te$

Group 17: $HF > HCl < HBr < HI$

Solubility

Hydrogen bonding also influences the solubility of substances in certain solvents. Covalent compounds, for instance, do not generally dissolve in water; however, those that can form a hydrogen bond with water readily dissolve in it. For example, alcohols like ethanol, ammonia, amines, lower aldehydes and ketones are soluble in water due to the formation of hydrogen bonds between the electronegative atom in these molecules with hydrogen atom of water molecules.

Anomalous Behavior of Water

The anamalous properties of water explained on the basis of hydrogen bonding:

1. Generally, density of the solid form of a compound is greater than its liquid form; and density of liquids decreases on heating. However, in case of water, the density of ice is less than that of water because of which ice always floats over water and the density of water increases from 0°C, reaches a maximum at 4°C and then decreases.

   This is because the water molecules are associated in groups due to intermolecular hydrogen bonding as shown in Fig. 6.29. In the solid state, the tetrahedral arrangement of H_2O molecules extends in three dimensions. Furthermore, the packing of molecules of H_2O is not very close due to hydrogen bond length being longer than covalent bond length between O and H. Hence in the open–cage-like crystal structure of ice, vacant spaces exist, resulting in a larger volume for the given mass of water in the solid state (ice). Thus, the density of ice is less than water.

2. On increasing temperature, when ice melts, the open-cage structure collapses due to partial breaking of the hydrogen bonds. The H_2O molecules come closer, and also fill the vacant spaces in the open-cage structure. This results in decrease of volume; hence, the density increases on heating above the melting point of ice and becomes maximum at 4°C.

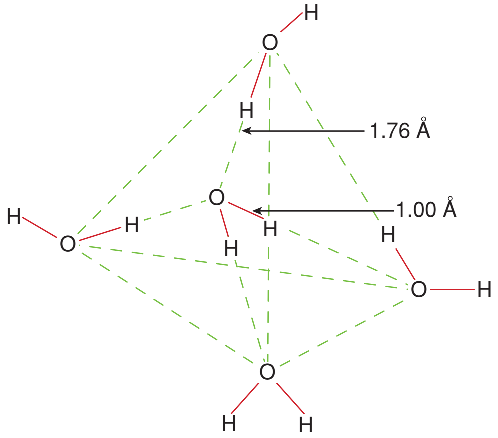


Figure 6.29 Tetrahedral arrangement of associated water molecules in ice.

Applications of Hydrogen Bond

Despite their low bond energy, hydrogen bonds are of great significance both in biochemical systems and in normal chemistry. Some important applications are listed as follows:

1. Hydrogen bonds are extremely important because they are responsible for linking polypeptide chains in proteins, and for linking pairs of bases in large nucleic acid-containing molecules. The hydrogen bonds maintain these large molecules in specific molecular configurations, which is important in the operation of genes and enzymes.
2. They are responsible for water being liquid at room temperature; but for this, life as we know it would not exist.
3. Since hydrogen bonds have low bond energy, they also have low activation energy, and this results in their playing an important part in many reactions at normal temperatures.
4. Intramolecular hydrogen bonds play an important role in maintaining the structure of biological materials, such as coiled and folded structures of proteins and the double helix of DNA. The two strands of the double helix in DNA are held together by hydrogen bonds between hydrogen atoms of one strand with the lone pairs on the nitrogen or oxygen on the other strand.

Solved Example 6-34

Arrange the following in the order of decreasing boiling point.

(a) NH_3, PH_3, AsH_3, SbH_3 **(b)** H_2O, H_2S, H_2Se, H_2Te

Solution

(a) The order of boiling point is $PH_3 > AsH_3 > NH_3 > SbH_3$. As we move down the group, doe to increase in atomic size, the van der Waal forces of attraction become stronger, thus M

Solved Example 6-36

Although electronegativity of N and Cl are same, but N shows hydrogen bonding and Cl not. Explain.

Solution

The size of N atom ($2s^2\ 2p^3$) is smaller than Cl atom ($3s^2\ 3p^3$). This gives rise to more electron density on N atom which is responsible for H bonding in addition to electronegativity.

Solved Example 6-37

Why KHF_2 exists but $KHCl_2$ does not?

Solution

In case of KHF_2, there is hydrogen bonding in HF which dissociate to give HF_2^- ion so, it exists. Whereas in case of $KHCl_2$, as we know that there is no hydrogen bonding in HCl molecule (Cl being bigger in size than H), it cannot dissociate into HCl_2^- and thus does not exist.

6.14 | MOLECULAR ORBITAL THEORY

In the molecular orbital theory, the valence electrons are considered to be associated with all the nuclei in the molecule. Thus, the atomic orbitals *from different atoms* must be combined to produce molecular orbitals. Developed by Friedrich Hund and Robert S. Mulliken in 1932, **molecular orbital theory** takes the view that a molecule is similar to an atom in one important respect. Both have energy levels that correspond to various orbitals that can be populated by electrons. In atoms, these orbitals are called atomic orbitals; in molecules, they are called **molecular orbitals** (**MOs**). The molecular orbital theory is based on the following assumptions:

1. When two atoms approach each other, their atomic orbitals lose their identity and mutually overlap to form new orbitals called molecular orbitals.
2. The molecular orbitals are polycentric and are associated with the nuclei of all the atoms constituting the molecule. The electron probability distribution around the group of nuclei constituting the molecule is given by the molecular orbitals just as atomic orbitals give probability of finding an electron around the nucleus in an atom.
3. Only atomic orbitals of about the same energy and same symmetry interact significantly.
4. The total number of molecular orbitals produced is always equal to the total number of atomic orbitals contributed by the atoms that have combined.
5. When two atomic orbitals overlap, they interact to form two molecular orbitals, in the following two ways:
   - **(a)** When the atomic orbitals overlap in-phase, it leads to an increase in the intensity of the negative charge in the region of overlap; the molecular orbital formed has lower potential energy than the separate atomic orbitals and is called a **bonding molecular orbital**.
   - **(b)** When the atomic orbitals overlap out-of-phase, it leads to a decrease in the intensity of the negative charge between the nuclei and leads to higher potential energy; molecular orbitals of this type are called **antibonding molecular orbitals**. Electrons in this type of molecular orbital destabilize the bond between atoms.
   - **(c)** The amount of stabilization of the bonding orbital equals the amount of destabilization of the antibonding orbital.
6. Electrons of the combining atoms are then assigned to these molecular orbitals. Each molecular orbital can accommodate a maximum of two electrons of successively higher energy according to Pauli's exclusion principle and Hund's rule of maximum multiplicity.

Formation of Molecular Orbitals by Linear Combination of Atomic Orbitals (LCAO)

One common mathematical approximation to generate molecular orbitals for some small diatomic molecules is called the linear combination of atomic orbitals (LCAO) approach. Consider two atoms A and B which have atomic orbitals described by the wave functions Ψ_A and Ψ_B. When the electron clouds of these two atoms overlap as the atoms approach, the wave function for the molecule can be obtained by a linear combination of the atomic orbitals Ψ_A and Ψ_B.

The atomic orbitals Ψ_A and Ψ_B combine to give rise to a pair of molecular orbitals Ψ_g and Ψ_u. The function Ψ_g corresponds to increased electron density in between the nuclei due to in-phase overlap and is, therefore, a bonding molecular orbital $[\Psi_g = \Psi_A + \Psi_B]$. It is lower in energy than the original atomic orbitals. The function Ψ_u corresponds to out-of-phase overlap, and hence corresponds to minimized electron density in between the nuclei. This is an antibonding molecular orbital which is higher in energy $[\Psi_u = \Psi_A - \Psi_B]$.

Suppose the atoms A and B are hydrogen atoms; then the wave functions Ψ_A and Ψ_B describe the 1*s* atomic orbitals on the two atoms. Two combinations of the wave functions Ψ_A and Ψ_B are possible (Fig. 6.30) where:

1. the signs of the two wave functions are the same.
2. the signs of the two wave functions are different.

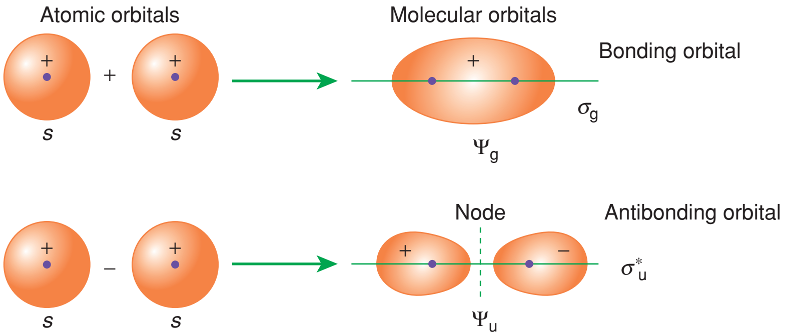


Figure 6.30 *s*–*s* combinations of atomic orbitals.

When a pair of atomic orbitals Ψ_A and Ψ_B combine, they give rise to a pair of molecular orbitals Ψ_g and Ψ_u. The number of molecular orbitals produced must always be equal to the number of atomic orbitals involved. The function Ψ_g leads to increased electron density in between the nuclei, and is therefore a bonding molecular orbital. It is lower in energy than the original atomic orbitals. Conversely, Ψ_u results in two lobes of opposite sign cancelling and hence giving zero electron density in between the nuclei. This is an antibonding molecular orbital which is higher in energy as shown in Fig. 6.31(a).

The molecular orbital wave functions are designated Ψ_g and Ψ_u; g stands for *gerade* (even) and u for *ungerade* (odd), and these refer to the symmetry of the orbital about its center. The energy of the bonding molecular orbital Ψ_g passes through a minimum [Fig. 6.31(a)], and the distance between the atoms at this point corresponds to the internuclear distance between the atoms when they form a bond.

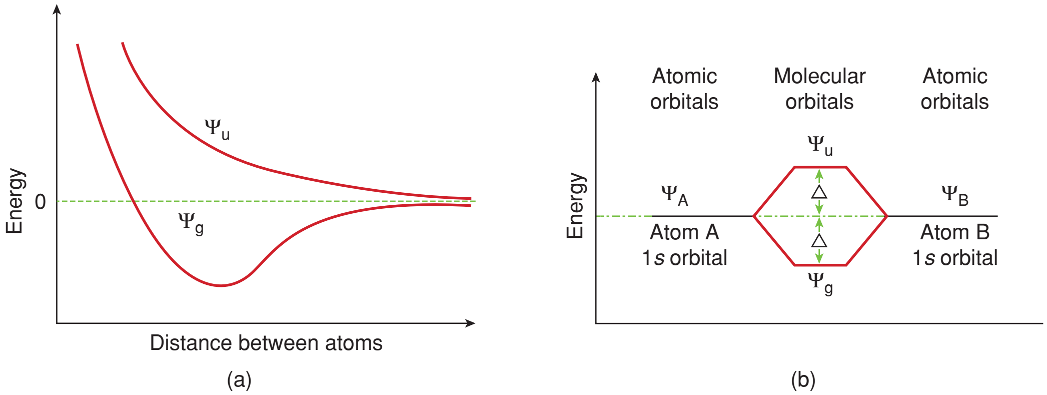


Figure 6.31 (a) Energy of Ψ_g and Ψ_u orbitals. (b) Energy levels of *s*–*s* atomic and molecular orbitals.

The energy of the bonding molecular orbital is lower than that of the atomic orbital by an amount Δ. This is known as the stabilization energy. Similarly the energy of the antibonding molecular orbital is increased by Δ. Atomic orbitals may hold up to two electrons (provided that they have opposite spins) and the same applies to molecular orbitals. In the case of two hydrogen atoms combining, there are two electrons to be considered: one from the 1*s* orbital of atom A and one from the 1*s* orbital of atom B. When combined, these two electrons both occupy the bonding molecular orbital Ψ_g. This results in a saving energy of 2Δ, which corresponds to the bond energy. It is only because the system is stabilized in this way that a bond is formed [Fig. 6.31(b)].

An *s* orbital may combine with a *p* orbital provided that the lobes of the *p* orbital are pointing along the axis joining the nuclei. When the overlapping lobes have the same sign, this gives a bonding MO with an increased electron density between the nuclei. When the overlapping lobes have opposite signs this gives an antibonding MO with a reduced electron density in between the nuclei (Fig. 6.32).

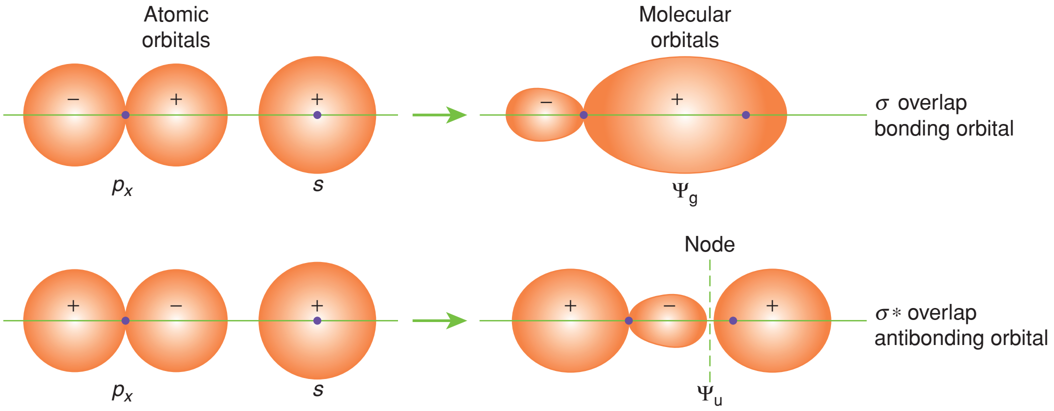


Figure 6.32 *s–p* combinations of atomic orbitals.

In the case of *p* orbitals, there are two different kinds of overlap possible, namely, end-on and side-on. End-on overlapping of two p_x atomic orbitals along the internuclear axis of the molecule creates σ (bonding) and σ^* (antibonding) molecular orbitals. While side-on overlap of p_y and p_z orbitals creates π (bonding) and π^* (antibonding) molecular orbitals.

The σ bonds are cylindrically symmetric to rotation about the bonding axis (the *x* direction) while π bonds lack cylindrical symmetry and have a node passing through the bonding axis. The σ and π bonding and antibonding molecular orbitals formed from the overlap of two *p* atomic orbitals are shown in Fig. 6.33.

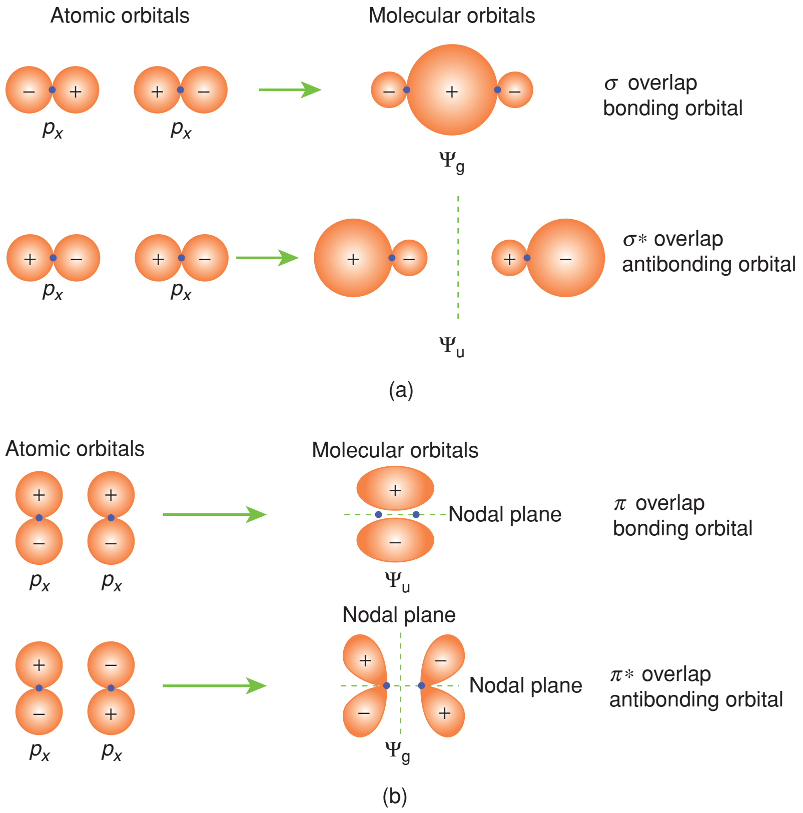


Figure 6.33 *p–p* combinations of atomic orbitals giving (a) σ bonding and (b) π bonding.

The distinguishing characteristics of bonding and antibonding orbitals are summarized in Table 6.11.

Table 6.11 Distinguishing characteristics of bonding and antibonding orbitals

Bonding orbitals	Antibonding orbitals
These are formed by in-phase overlap of atomic orbitals $[\Psi_A + \Psi_B]$. In a bonding MO, there is an increased electron density between the nuclei.	These are formed by out-of-phase overlap between atomic orbitals $[\Psi_A - \Psi_B]$. In an antibonding MO, there is a reduced electron density in between the nuclei.
The energy of the bonding molecular orbital is lower than that of the atomic orbital from which it is formed.	The energy of the antibonding molecular orbital is higher than that of the atomic orbital from which it is formed.
The electrons present in them result in attraction between the combining atoms.	The electrons present in them result in repulsion between the combining atoms.
These are represented by σ and π.	These are represented by σ^* and π^*.

Conditions for the Combination of Atomic Orbitals

In deciding which atomic orbitals may be combined to form molecular orbitals, three rules must be considered:

1. The atomic orbitals must be roughly of the same energy. This is important when considering overlap between two different types of atoms.
2. The orbitals must overlap one another as much as possible. This implies that the atoms must be close enough for effective overlap and that the radial distribution functions of the two atoms must be similar at this distance.
3. In order to produce bonding and antibonding MOs, either the symmetry of the two atomic orbitals must remain unchanged when rotated about the internuclear line, or both atomic orbitals must change symmetry in an identical manner.

Types of Molecular Orbitals

The molecular orbitals formed from the linear combinations of the atomic orbitals can thus be represented as shown in Table 6.12.

Table 6.12 Atomic and molecular orbitals

Atomic Orbitals	$1s_A + 1s_B$	$1s_A - 1s_B$	$2s_A + 2s_B$	$2s_A - 2s_B$	$2p_{xA} + 2p_{xB}$	$2p_{xA} - 2p_{xB}$	$2p_{yA} + 2p_{yB}$	$2p_{yA} - 2p_{yB}$	$2p_{zA} + 2p_{zB}$	$2p_{zA} - 2p_{zB}$
Molecular Orbitals	$\sigma 1s$	$\sigma^* 1s$	$\sigma 2s$	$\sigma^* 2s$	$\sigma 2p_x$	$\sigma^* 2p_x$	$\pi 2p_y$	$\pi^* 2p_y$	$\pi 2p_z$	$\pi^* 2p_z$

Energy Level Diagram for Molecular Orbitals

The diagram showing the relative energy levels of the combining atomic orbitals, the molecular orbitals formed from them and the order of filling up of the electrons is called the molecular orbital (MO) diagram. The orbitals of the individual combining atoms are written on either side of the diagram as horizontal lines at heights denoting their relative energies. The electrons in each atomic orbital are represented by arrows. The molecular orbitals of the molecule are represented in the middle of the diagram. Dashed lines connect the parent atomic orbitals with the molecular orbitals.

The order of energy of molecular orbitals has been determined mainly from spectroscopic data. In simple homonuclear diatomic molecules, the order is:

$$\underset{\xrightarrow{\text{Increasing energy}}}{\sigma 1s, \sigma^* 1s, \sigma 2s, \sigma^* 2s, \sigma 2p_z, \left\{\begin{matrix}\pi 2p_x, \\ \pi 2p_y,\end{matrix}\right. \left\{\begin{matrix}\pi^* 2p_x, & \sigma^* 2pz \\ \pi^* 2p_y & \end{matrix}\right.} \tag{6.7}$$

The bonding $\pi 2p_x$ and $\pi 2p_y$ MOs have exactly the same energy and are said to be doubly degenerate. In a similar way, the antibonding π^*2p_x and π^*2p_y MOs have the same energy and are also doubly degenerate.

A similar arrangement of MOs exists from $\sigma 3s$ to σ^*3p_x, but the energies are known with less certainty. The energies of the $\sigma 2p$ and $\pi 2p$ MOs are very close together. The order of MOs shown above is correct for oxygen and heavier elements; but for the lighter elements boron, carbon and nitrogen the $\pi 2p_x$ and $\pi 2p_y$ are probably lower than $\sigma 2p_z$. For these atoms the order is:

$$\underrightarrow{\sigma 1s,\ \sigma^*1s,\ \sigma 2s,\ \sigma^*2s,\ \begin{cases}\pi 2p_x, \\ \pi 2p_y\end{cases} \sigma 2p_z, \sigma^*2p_z,\ \begin{cases}\pi^*2p_x \\ \pi^*2p_y\end{cases}} \quad (6.8)$$

$$\xrightarrow{\text{Increasing energy}}$$

The molecular orbital diagram representing the order of energy levels for second period diatomic molecules is shown in Fig. 6.34.

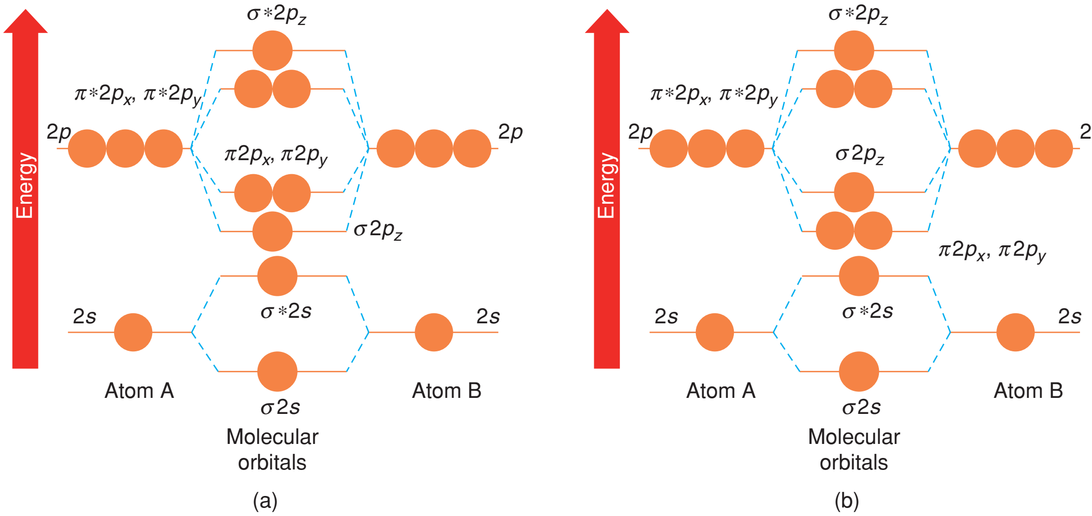


Figure 6.34 Approximate relative energies of molecular orbitals in second period diatomic molecules: (a) O_2 through Ne_2; (b) Li_2 through N_2.

6.15 | CONCEPT OF BOND ORDER, BOND LENGTH AND BOND ENERGY

The molecular orbitals are filled with the total number of electrons (not just the valence electrons) counted by taking the atomic number of both the atoms of the covalent bond. The electrons are filled from the lowest energy orbital in the order of increasing energy and orbitals of equal energy are half-filled with parallel spin before they begin to pair up. The distribution of electrons in various molecular orbitals is known as electronic configuration of the molecule. The electronic configuration provides important information about the stability and nature of bonds in the molecules.

Stability of the Molecules

The stability of molecules can be determined by the relative number of electrons in the bonding (N_b) and non-bonding (N_a) molecular orbitals.

1. The molecule is stable if $N_b > N_a$. Since greater number of bonding orbitals are occupied, the bonding is stronger and the molecule is more stable.
2. The molecule is unstable if $N_b < N_a$. Since greater number of antibonding orbitals is occupied, the antibonding influence is stronger and the molecule is unstable.

Bond order is defined as the number of pairs of electrons shared between two atoms. Molecular orbital theory also predicts the bond order and hence the qualitative bond strength between covalently bonded atoms, which is given by:

$$\text{Bond order} = \frac{1}{2}(N_b - N_a) \tag{6.9}$$

where N_b and N_a are the number of electrons in the bonding and antibonding molecular orbitals. Thus, in terms of molecular orbitals, bond order can be defined as one half of the difference between the number of electrons present in the bonding and the antibonding orbitals. The stability of the molecules can be related to bond order in the following terms:

1. A positive bond order ($N_b > N_a$) implies that the molecule is stable.
2. A negative ($N_b < N_a$) or zero ($N_b = N_a$) value of bond order implies that the molecule is unstable. The value of the bond order is indicative of the **nature of bond**. Integral values 1, 2 or 3 correspond to single, double or triple bond.
3. If two molecules or ions have the same bond order, then the molecule or ion with lower number of electrons in the antibonding molecular orbitals (ABMO) is more stable.

Let us consider the following examples to understand the relation between number of electrons in bonding and non-bonding molecular orbitals and nature of bonds in the molecule. For the H_2 molecule, we have

$$\text{Bond order} = \frac{2-0}{2} = 1$$

A bond order of 1 corresponds to a single bond. For He_2 we have

$$\text{Bond order} = \frac{2-2}{2} = 0$$

A bond order of zero means there is no bond, so the He_2 molecule is unable to exist. For the He_2^+ ion, which is able to form, the calculated bond order is

$$\text{Bond order} = \frac{2-1}{2} = 0.5$$

Notice that the bond order does not have to be a whole number. In this case, it indicates a bond character equivalent to about half a bond.

Bond length is the distance between the nucleus of atoms involved in bonding. These are aslo known as bond distances. The bond order between two atoms in a molecule can also be taken as approximate measure of its **bond length**. The bond length decreases with increase in bond order.

The amount of energy required to break a bond is called bond dissociation energy or simply **bond energy**. The bond energies of similar bonds having similar bond lengths is also consistent. It is the measure of strength of a bond. Higher the bond energy, the bond will be stronger. For shorter bonds such as double and triple bonds, the bond energy is high.

The relation between bond order, bond length and bond energy can be summarized as follows:

$$\text{Lower bond order} \Rightarrow \text{Longer bond length} \Rightarrow \text{Lower bond energy} \Rightarrow \text{Weaker bond}$$

$$\text{Higher bond order} \Rightarrow \text{Shorter bond length} \Rightarrow \text{Higher bond energy} \Rightarrow \text{Stronger bond}$$

Magnetic Properties

The MO theory has been very useful and successful in predicting the magnetic behavior of molecules. In filling up the molecular orbitals, if a molecule contains no unpaired electrons then it is diamagnetic and if it contains one or more unpaired electrons, then it is paramagnetic.

Solved Example 6-38

On the basis of ground sate electronic configuration arrange the following molecules in increasing O–O bond length order. KO_2, O_2 and $O_2[AsF_6]$ **(IIT-JEE 2004)**

Solution

In KO_2, the anion is O_2^- with electronic configuration

$$\sigma 1s^2\ \sigma^*1s^2\ \sigma 2s^2\ \sigma^*2s^2\ \sigma 2p_z^2\ \pi 2p_x^2 = \pi 2p_y^2\ \pi^*2p_x^2 = \pi^*2p_y^1$$

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{10-7}{2} = \frac{3}{2}$$

The electronic configuration of O_2 is $\sigma 1s^2\ \sigma^*1s^2\ \sigma 2s^2\ \sigma^*2s^2\ \sigma 2p_z^2\ \pi 2p_x^2 = \pi 2p_y^2\ \pi^*2p_x^1 = \pi^*2p_y^1$

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{10-6}{2} = \frac{4}{2} = 2$$

In $O_2[AsF_6]$, the anion is O_2^+ with electronic configuration

$$\sigma 1s^2\ \sigma^*1s^2\ \sigma 2s^2\ \sigma^*2s^2\ \sigma 2p_z^2\ \pi 2p_x^2 = \pi 2p_y^2\ \pi^*2p_x^1 = \pi^*2p_y^0$$

$$\text{Bond order} = \frac{10-5}{2} = \frac{5}{2} = 2.5$$

Bond length is inversely proportional to bond order. So, Bond length order is $O_2^+ < O_2 < O_2^-$.

Solved Example 6-39

Arrange the species O_2, O_2^-, O_2^{2-} and O_2^{2+} in the decreasing order of bond order and stability and also indicate their magnetic properties.

Solution

The molecular orbital configuration of O_2, O_2^-, O_2^{2-} and O_2^{2+} are as follows:

$$O_2 = \sigma 1s^2\ \sigma^*1s^2\ \sigma 2s^2\ \sigma^*2s^2\ \sigma 2p_x^2\ \pi 2p_y^2\ \pi 2p_z^2\ \pi^*2p_y^1 = \pi^*2p_z^1$$

$$\text{Bond order} = \frac{10-6}{2} = 2$$

As the number of unpaired electrons = 2, so the compound O_2 is paramagnetic.

$$O_2^- = \sigma 1s^2\ \sigma^*1s^2\ \sigma 2s^2\ \sigma^*2s^2\ \sigma 2p_z^2\ \pi 2p_x^2 = \pi 2p_y^2\ \pi^*2p_x^2 = \pi^*2p_y^1$$

$$\text{Bond order} = \frac{10-7}{2} = 1.5$$

As the number of unpaired electron = 1, so the compound O_2^{2-} is paramagnetic.

$$O_2^{2-} = \sigma 1s^2, \sigma^*1s^2, \sigma 2s^2, \sigma^*2s^2, \sigma 2p_x^2, \pi 2p_y^2, \pi 2p_z^2, \pi^*2p_y^2 = \pi^*2p_z^2$$

$$\text{Bond order} = \frac{10-8}{2} = 1$$

The number of unpaired electrons = 0, so the compound O_2^{2-} is diamagnetic.

$$O_2^+ = \sigma 1s^2\ \sigma^*1s^2\ \sigma 2s^2\ \sigma^*2s^2\ \sigma 2p_x^2\ \pi 2p_y^2\ \pi 2p_z^2\ \pi^*2p_y^1 = \pi^*2p_z^0$$

$$\text{Bond order} = \frac{10-5}{2} = 2.5$$

The number of unpaired electrons = 1, so the compound is paramagnetic.

6.16 | BONDING IN SOME HOMONUCLEAR DIATOMIC MOLECULES

1. **Hydrogen molecule (H_2):** The MO diagram for the simplest molecule, H_2, is shown in Fig. 6.35.

The two hydrogen atoms with one electron each in 1*s* atomic orbitals combine to form $\sigma 1s$ (bonding) σ^*1s (antibonding) molecular orbitals; the two electrons fill a single bonding $\sigma 1s$ molecular orbital. The energies of the separate 1*s* atomic orbitals are indicated at the left and right; those of the molecular orbitals are shown in the center.

The configuration of the H_2 molecule is written as $\sigma 1s^2$. As the H_2 molecule has one electron pair in its bonding orbital and none in its antibonding orbital, molecular orbital theory predicts that H_2 has a bond order of 1 [(1/2) (2 – 0) = 1] and is diamagnetic as there are no unpaired electrons.

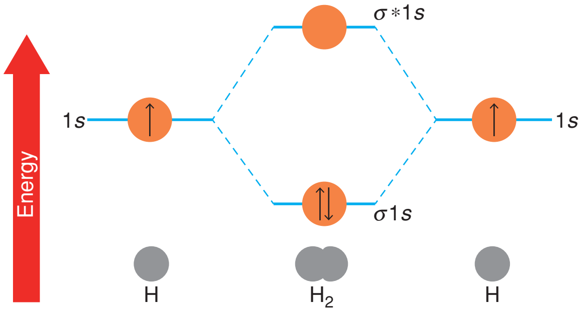


Figure 6.35 MO diagram of H_2.

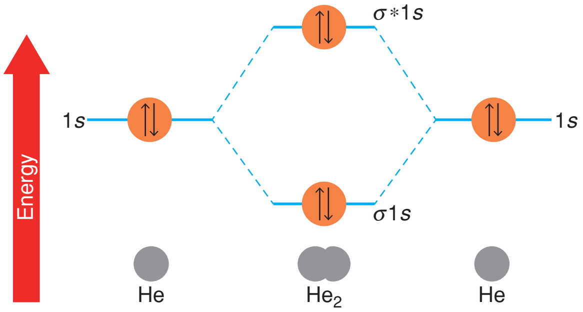


Figure 6.36 MO diagram of He_2.

2. **Helium molecule (He_2):** It can be seen from the MO diagram that the configuration of He_2 is $(\sigma 1s)^2$ $(\sigma^* 1s)^2$; the amount of stabilization due to filling of two electrons in the bonding orbital is equal to the amount of destabilization due to the two electrons in the antibonding molecular orbital. Notice that both bonding and antibonding orbitals are filled. In situations such as this, there is a net destabilization because the antibonding MO is raised in energy more than the bonding MO is lowered, relative to the orbitals of the separated atoms. This means the total energy of He_2 is larger than that of two separate He atoms, so the "molecule" is unstable and immediately comes apart. There is no net stabilization due to bonding so the *He_2 molecule will not exist*. The bond order calculation also shows that the bond order is zero [(1/2) (2 – 2) = 0] for the He_2 molecule. The MO theory thus gives exactly the same prediction for He_2 as is observed – that helium is a noble gas and does not form covalent compounds (Fig. 6.36).

> **Note:** In general, the effects of **antibonding electrons** (those in antibonding MOs) cancel the effects of an equal number of bonding electrons, and molecules with equal numbers of bonding and antibonding electrons are unstable. If we remove an antibonding electron from He_2 to give He_2^+, there is a net excess of bonding electrons, and the ion should be capable of existence. In fact, the emission spectrum of He_2^+ can be observed when an electric discharge is passed through a helium-filled tube, which shows that He_2^+ is present during the electric discharge. However, the ion is not very stable and cannot be isolated.

3. **Lithium molecule (Li_2):** Each Li atom has two electrons in its inner shell, and one in its outer shell, giving three electrons. Thus, there is a total of six electrons in the molecule, and these are arranged in MOs: $\sigma 1s^2$, $\sigma^* 1s^2$, $\sigma 2s^2$. The inner shell of filled $\sigma 1s$ and $\sigma^* 1s$ MOs do not contribute to the bonding in much the same way as in He_2. They are essentially the same as the atomic orbitals from which they were formed, and are sometimes written as: KK, $\sigma 2s^2$. The bond order of Li_2 is (1/2) (4 – 2) = 1. This implies that Li_2 molecule is stable and the molecules are found to exist in the vapor state. However, in the solid it is energetically more favorable for lithium to form a metallic structure. Since there is no unpaired electron, the molecule is diamagnetic.
4. **Carbon molecule (C_2):** A carbon atom has 2 + 4 electrons. A C_2 molecule would contain a total of 12 electrons, and these would be arranged in MOs:

$$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \left\{ \begin{array}{l} \pi 2p_x^2 \\ \pi 2p_y^2 \end{array} \right.$$

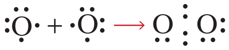
The bond order is (1/2) (8 – 4) = 2. Since the bond order is 2, the molecule should be stable and exist as diamagnetic molecule C_2. It is important to note here that the two bonds between carbon atoms are both π bonds because of the presence of four electrons in two π molecular orbitals. This is different from usual double bonds that are constituted by a σ and π bond. In fact, carbon exists as a macromolecule in graphite and diamond, since these are an even more stable arrangements (where each carbon forms four bonds); hence diamond and graphite are formed in preference to C_2.

5. **N_2 molecule:** A nitrogen atom has 2 + 5 = 7 electrons. Thus, the N_2 molecule contains 14 electrons. These are arranged in MOs:

$$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \left\{ \begin{array}{l} \pi 2p_x^2 \\ \pi 2p_y^2 \end{array} \right. \sigma 2p_z^2$$

Assuming that the inner shell does not participate in bonding, and that the bonding and antibonding 2*s* levels cancel, one σ and two π bonding pairs remain, giving a total of three bonds. This is in agreement with the valence bond formulation as N≡N.

6. **Oxygen molecule (O_2):** Molecular orbital theory is particularly successful in explaining the electronic structure of the oxygen molecule. Experiments show that O_2 is paramagnetic (it is weakly attracted to a magnet) and that the molecule contains two unpaired electrons. In addition, the bond length in O_2 is about what is expected for an oxygen–oxygen double bond. Lewis electron pair theory or the valence bond theory, these do not predict unpaired electrons or paramagnetism.



Each oxygen atom has 2 + 6 = 8 electrons. Thus, the O_2 molecule contains a total of 16 electrons. These are arranged in MOs:

$$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \begin{cases} \pi 2p_x^2, \\ \pi 2p_y^2, \end{cases} \begin{cases} \pi^* 2p_x^1 \\ \pi^* 2p_y^1 \end{cases}$$

The antibonding π^*2p_x and π^*2p_y orbitals are singly occupied in accordance with Hund's rule. Unpaired electrons give rise to paramagnetism. Since there are two unpaired electrons with parallel spins, this explains why dioxygen is paramagnetic.

The inner shell does not participate in bonding and the bonding and antibonding 2*s* orbitals cancel each other. A σ bond results from the filling of $\sigma 2p_z^2$. Since $\pi^* 2p_x^1$ is half-filled and, therefore, cancels half the effect of the completely filled $\pi 2p_x^2$ orbital, half of a π bond results. Similarly, another half of a π bond arises from $\pi 2p_y^2$ and $\pi^* 2p_y^1$, giving a total of $1+\frac{1}{2}+\frac{1}{2}=2$ bonds. The bond order is, thus, 2. Instead of working out the bond order by cancelling the effects of filled bonding and antibonding MOs, the bond order may be calculated as half the difference between the number of bonding and antibonding electrons. In the case of O_2 the bond order calculates as $(10-6)/2 = 2$, which corresponds to a double bond.

Applying these rules to the valence electrons of the second period elements gives the MO electron configurations shown in Table 6.13. The molecular orbital theory can generally account for the data that are available for these molecules.

Table 6.13 Molecular orbital populations and bond orders for diatomic molecules of the second period[a]

		Li_2	Be_2	B_2	C_2	N_2			O_2	F_2	Ne_2
Energy ↑	σ^*2p_z	○	○	○	○	○	Energy ↑	σ^*2p_z	○	○	⇅
	π^*2p_x, π^*2p_y	○○	○○	○○	○○	○○		π^*2p_x, π^*2p_y	↑↑	⇅⇅	⇅⇅
	$\sigma 2p_z$	○	○	○	○	⇅		$\pi 2p_x$, $\pi 2p_y$	⇅⇅	⇅⇅	⇅⇅
	$\pi 2p_x$, $\pi 2p_y$	○○	○○	↑↑	⇅⇅	⇅⇅		$\sigma 2p_z$	⇅	⇅	⇅
	σ^*2s	○	⇅	⇅	⇅	⇅		σ^*2s	⇅	⇅	⇅
	$\sigma 2s$	⇅	⇅	⇅	⇅	⇅		$\sigma 2s$	⇅	⇅	⇅
Number of bonding electrons		2	2	4	6	8			8	8	8
Number of antibonding electrons		0	2	2	2	2			4	6	8
Bond order		1	0	1	2	3			2	1	0
Bond enthalpy (kJ mol^{-1})		110	–	300	612	953			501	129	–
Bond length (pm)		267	–	158	124	109			121	144	–

[a] Although the order of the energy levels corresponding to the $\sigma 2p_x$, and the π bonding MOs become reversed at oxygen, either sequence would yield the same result – a triple bond for N_2, a double bond for O_2, and a single bond for F_2.

According to Table 6.13, MO theory predicts that molecules of Be_2 and Ne_2 should not exist at all because they have bond orders of zero. In beryllium vapor and in gaseous neon, no evidence of Be_2 or Ne_2 has ever been found. MO theory also predicts that diatomic molecules of the other second period elements should exist because they all have bond orders greater than zero. These molecules have, in fact, been observed. Although lithium, boron, and carbon are complex solids under ordinary conditions, they can be vaporized. In the vapor, molecules of Li_2, B_2, and C_2 can be detected. Nitrogen, oxygen and fluorine, as you know, are gaseous elements that exist as N_2, O_2 and F_2.

In Table 6.13, the predicted bond order increases from boron to carbon to nitrogen and then decreases from nitrogen to oxygen to fluorine. As the bond order increases, the *net* number of bonding electrons increases, so the bonds should become stronger and the bond lengths shorter. The *experimentally measured* bond energies and bond lengths given in Table 6.13 agree with these predictions quite nicely. The salient features of valence bon theory and molecular orbital theory are compared and contrasted in Table 6.14.

Table 6.14 Salient features of valence bond theory and molecular orbital theory

Valence bond theory	Molecular orbital theory
Bond formation takes place due to overlap of atomic orbitals.	Bond formation takes place due to overlap of molecular orbitals formed by overlap of atomic orbitals.
Overlap occurs in atomic orbitals of comparable energy and symmetry.	Overlap to form molecular orbitals occurs in atomic orbitals of similar energy and symmetry.
The atomic orbital retain their individual characters to a large extent	The atomic orbitals that combine to form molecular orbital lose their identity completely.
The electrons are present in the atomic or hybridized atomic orbitals.	The electrons of the molecule are present in the molecular orbitals which are filled just as atomic orbitals are filled with electrons.
It can explain the directional properties of bonds and the shapes of molecules	It can explain the directional properties of bonds and the shapes of molecules
It cannot explain parmagnetism of O_2 molecule.	It can explain paramagnetism of O_2 molecule.
It uses concept of resonance to explain nature of bond in some molecules.	It does not use concept of resonance.
It fails to predict and explain existence of He_2^+	It predicts and explains the existence of He_2^+

6.17 | HETERONUCLEAR DIATOMIC MOLECULES

The MO theory can also be extended to heteronuclear diatomic molecules, that is, molecules that consist of two dissimilar atoms, such as HF, CO, NO, etc. The atomic orbitals of the two different atoms involved in bonding are now at different energy levels; the atom with higher electronegativity will have its atomic orbitals at lower energy, making a larger contribution to the bonding molecular orbital. The atomic orbital with the higher energy makes a larger contribution to the antibonding molecular orbital. However, there is no interaction if the energy difference between orbitals is greater than 13 eV.

The electrons of the covalent bond in such molecules are no longer evenly shared between the two atoms, because it is energetically favorable for the electron pair to reside closer to one nucleus than to the other. This means that the chemical bond is polarized. For example, $H^{\delta+}–F^{\delta-}$ electron pair is located closer to the F nucleus than to the H nucleus.

The atomic orbitals in heteronuclear molecules combine together only if all the following conditions are satisfied:

1. They have the correct symmetry.
2. There is efficient overlap.
3. The orbitals are relatively close together in energy.

Heteronuclear diatomic molecules can have non-bonding orbitals, in addition to bonding and antibonding orbitals. Consider the following examples:

1. **HF molecule:** The atomic orbital energy levels are: hydrogen 1*s* (–13.61 eV), fluorine 2*s* (–40.17 eV) and 2*p* (–18.65 eV). In this case, there is no *s*-orbital interaction, because energy difference > 13 eV. The orbitals of 1*s* of hydrogen and $2p_x$ of fluorine can overlap to form a σ orbital due to compatible symmetry; while 1*s*, $2p_y$ and $2p_z$ of fluorine have no net overlap and are non-bonding. The MO diagram is as shown in Figure 6.37.

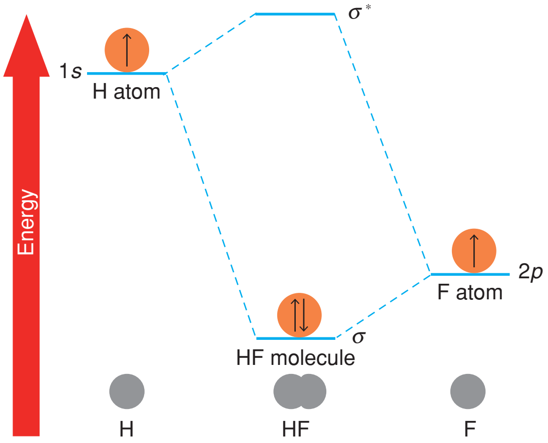


Figure 6.37 MO diagram of HF.

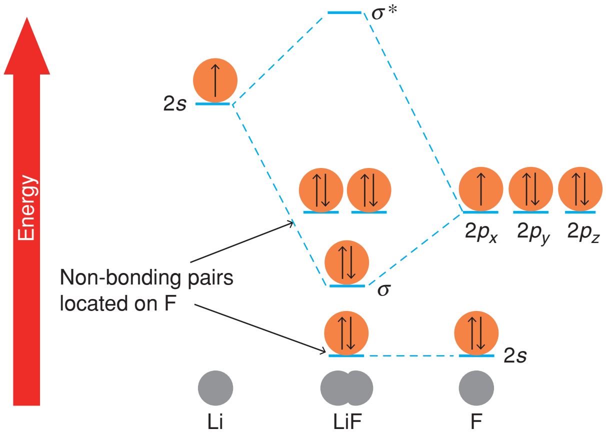


Figure 6.38 MO diagram of LiF.

2. **Li–F molecule:** The electrons in the Li–F bond are quite close in energy to fluorine's 2*p* orbitals. The bonding molecular orbital is primarily obtained by the interaction between 2*s* of lithium and $2p_x$ orbital of fluorine. The electrons in $2p_y$ and $2p_z$ orbitals on F that cannot bond with Li remain on F as lone pairs since fluorine is more electronegative than lithium. The electrons are more stable with lower energy, when they remain as lone pairs on fluorine rather than on lithium. So the MO diagram (Figure 6.38) predicts that the bond should be polarized towards fluorine.

   The construction of correlation diagrams of other heteronuclear diatomic orbitals follows exactly the same principles as those employed for LiF. The more electronegative element's orbitals are placed lower on the correlation diagram than those of the more electropositive element.

3. **CO molecule:** The MO diagram (Fig. 6.39) for the diatomic carbon monoxide (CO) shows that it is isoelectronic with nitrogen (N_2).

   The heteronuclear diatomic ions such as cyanide ion, CN^-, and nitrosonium ion, NO^+, are also isoelectronic with nitrogen, N_2. The only difference in their MO diagrams lies in the relative energies of the orbitals.

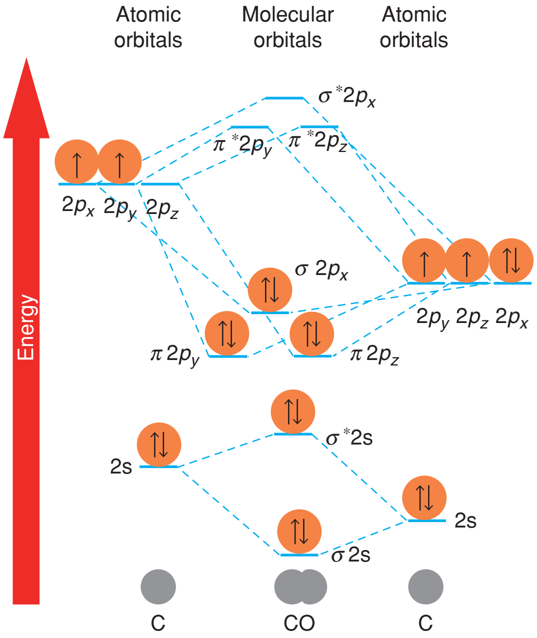


Figure 6.39 MO diagram of CO.

6.18 | ELEMENTARY IDEA OF METALLIC BONDING

The theory of covalent bonding cannot be extended to explain the bonding mechanism in metals. This is because the individual atoms of a metal do not have enough valence electrons to share and form an octet. Thus, another theory was proposed to explain the force of attraction holding the atoms together in a piece of metal which is called the *metallic bond*. The metallic bond can account for most of the physical characteristics of metals such as strength, malleability (ability to be hammered into sheets), ductility (ability to be drawn into wires), luster and conductance of heat and electricity.

Electron Sea Model

In the case of metals, in which the valence electrons are not tightly bound to the nucleus, every atom achieves a more stable configuration by sharing the outer shell electrons with the various other atoms in the metal lattice. Quantum mechanically, atomic orbitals on all the atoms overlap to give a vast number of molecular orbitals which extend over the whole metal. Hence, the valence electrons become detached from their parent atom and move freely amongst all the atoms within the crystal. In other words, the electrons are said to be *delocalized*. The metal lattice is held together by the strong forces of attraction between the positive nuclei and the delocalized electrons. This is described as "an array of positive ions in a sea of electrons" (Fig. 6.40).

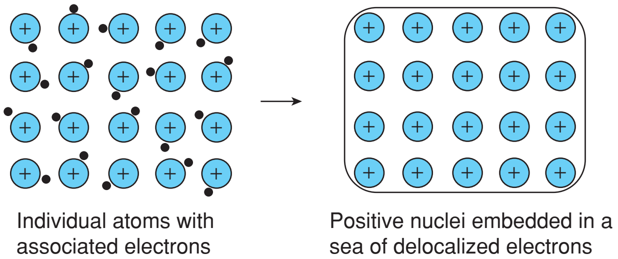

Individual atoms with associated electrons
Positive nuclei embedded in a sea of delocalized electrons

Figure 6.40 Electron sea model.

The strength of the metallic bond depends on the number of valence electrons contributed by the atoms to the delocalized electrons and the packing arrangement of the metal atom. More number of delocalized electrons and more closely packed atoms result in a stronger bond and a higher melting point. This explains why Group I metals have relatively low melting points compared to other metals. Since these metals have only one electron to contribute to the delocalized "sea" of electrons, are inefficiently packed and have large atomic radii, the delocalized electrons are farther away from the nucleus resulting in a weaker metallic bond.

The properties of the metals like malleability and ductility can be explained as the ability of the individual atoms to "slip" past one another, while being firmly held together by the electrostatic forces exerted by the electrons. As the electrons are delocalized over the positive ions and can move freely, metals exhibit good electrical conductivity. Heat conduction in metals can also be explained using the same principle – the free electrons can transfer the energy at a faster rate than those which are covalently bonded having their electrons fixed in position.

Metals typically have a shiny, metallic luster because photons of light do not penetrate very far into the surface of a metal and are typically reflected, or bounced off from the metallic surface.

Band Theory or Molecular Orbital Theory

Molecular orbital theory may be extended to explain bonding in metals and is known as the band theory. Consider the example of a piece of sodium metal. Each sodium atom has a single 3*s* valence electron. When two atoms are close together, the atomic orbitals will combine to form two molecular orbitals, 3σ and $3\sigma^*$. The two electrons will occupy the bonding molecular orbital, while the antibonding orbital will remain empty. Similarly for three sodium atoms, three molecular orbitals are formed – bonding, non-bonding and antibonding. When four sodium atoms combine, we get two 3σ orbitals and two $3\sigma^*$ orbitals. The quantum mechanical considerations do no permit these orbitals to be degenerate but they are closely placed, being almost similar in energy. The concept can be extended to *n* number of sodium atoms present in a piece of sodium metal. In this multi-atom system, the number of molecular orbital states will be equal to the number (n) of the atomic orbitals combining. Since the number of molecular orbitals is large, the spacing between them decreases to become almost negligible and we get a "band" of continuous energy levels (Fig. 6.41). These molecular orbitals extend in all three dimensions over all the atoms in the metal piece.

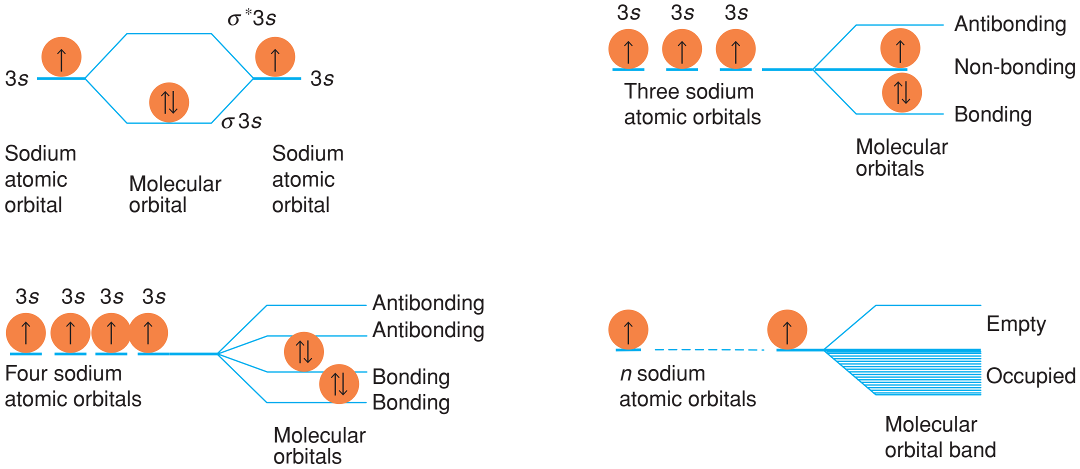


Figure 6.41 MO diagram for 2, 3 and *n* sodium atoms.

The molecular orbital theory can explain most of the physical properties of metals. Since the energy levels are closely spaced, a very small amount of energy is required for the electrons to rise from filled orbitals to the unoccupied orbitals. The electrons have high degree of mobility and this explains the high electrical and thermal conductivity of metals. In presence of an electric field, the mobile electrons, which move in all directions in absence of a field, begin to move towards the anode, causing electric current to flow. Similarly when the metal is heated, the mobile electrons gain energy and move towards the colder part of the metal, thus transferring heat. The metallic luster arises because of absorption of light of any wavelength by metal atoms on the surface and its re-emission. The electrons absorb light, move to higher energy levels and then emit the same amount of light to come back to the ground state. The presence of a band of energy levels in metals offers infinite number of such possible transitions between energy levels.

Band theory can also successfully explain the classification of materials into conductors, insulators and semiconductors. This results from the difference in the gap between the filled/partially filled valence band and the unfilled conduction band (Fig. 6.42).

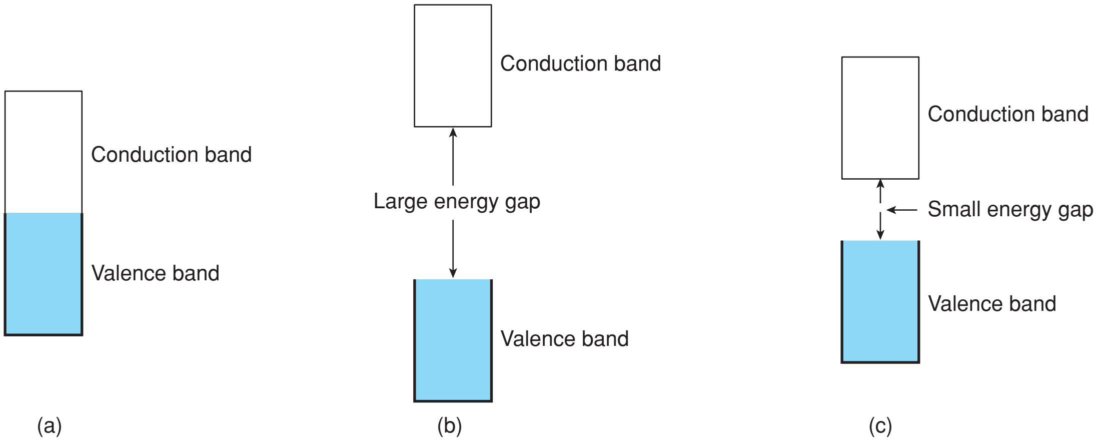


Figure 6.42 Valence and conduction band in (a) conductors, (b) insulators and (c) semiconductors.

1. In conductors, there is an overlap of valence and conduction bands; and the electrons from the valence band move effortlessly between the two bands. The electrons can thus move easily throughout the solid, making it a good conductor.
2. In insulators, the valence and conduction bands are widely separated and exist as distinct bands. The valence orbitals are filled so there is no movement of electrons possible, while the conduction band being empty, there are no electrons to move. Also, due to difference in the energy gap, a large amount of energy is required to promote the electrons from valence band to conduction band. So effectively there are no mobile charge carriers and hence insulators or non-metals do not conduct electricity.
3. In semiconductors, the valence and conduction bands are so placed that some amount of electrons can be excited to the upper vacant conduction band. Only a moderate amount of energy is required to promote electrons from the filled valence band to the empty conduction band. Semiconductors thus conduct electricity with some input of external energy. Also, since increase in temperature will increase the promotion of electrons to the conduction band, the conductivity of semiconductors increases with increase in temperature. Another way of increasing conductivity of semiconductors is through doping, which is discussed in Chapter 4.

6.19 | WEAK FORCES

There are three types of intermolecular forces which are together known as van der Waals forces of attraction. These are discussed as follows:

1. **Dipole-dipole or Keesom forces:** These forces arise due to dipolar nature of molecules. The opposite ends of the dipole are attracted electrostatically as shown in Fig 6.43.

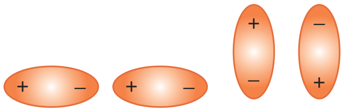


Figure 6.43 Dipole-dipole interactions.

2. **Dipole-induced dipole or Debye forces:** These arise when a dipole is kept near a non-polar molecule. It can induce a dipole moment in the adjacent no- polar molecules and this induced dipole then interacts with the dipole (Fig. 6.44).
3. **Instantaneous dipole-induced dipole interaction or London forces:** In molecules like X_2 (X = H, F, O, N, Cl, etc.) which have no permanent dipole, the atoms or molecules are attracted towards each other. In such molecules, at a given time, there is an instantaneous dipole in one of the molecule which induces dipole in the non-polar molecule. This type of interaction is illustrated by means of hydrogen molecule as an example, as shown in Figs. 6.45 (a) and (b).

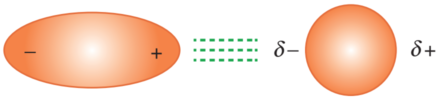
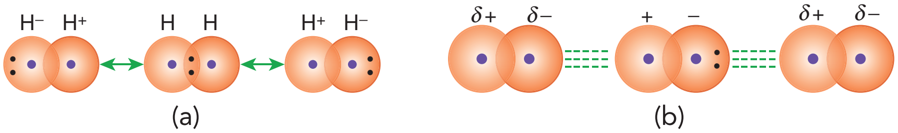


Figure 6.44 Dipole-induced dipole interactions.



(a) (b)

Figure 6.45 Instantaneous dipole-induced dipole interaction in hydrogen atom. (a) Electronic distribution. (b) Instantaneous dipole-induced dipole interaction.

Based on these three types of interactions, the following order on melting and boiling points are observed

1. $I_2 > Br_2 > Cl_2 < F_2$
2. He < Ne < Ar < Kr < Xe
3. $PbH_4 > SnH_4 > GeH_4 > SiH_4 > CH_4$
4. $CH_2 < C_2H_6 < C_3H_6 <$ …. (Homologous series)
5. HCl < HBr < HI
6. $H_2S < H_2Se < H_2Te$
7. $PH_3 < AsH_3 < SbH_3$
8. $H_2 < D_2 < T_2$

If molecular weight is the same, then molecular surface area is the dominating factor for determining boiling or melting point. For example,

Order of boiling points: *n*-pentane > iso-pentane > neo-pentane
Order of melting point: neo-pentane > iso-pentane > *n*-pentane)

Repulsive Intermolecular Forces

When molecules come close, the van der Waal's attractive forces increase but beyond a point electron and nucleus repulsion also increase and so does the repulsive forces. Eventually, there is an equilibrium established between attractive and repulsive forces. The repulsive energy is given by

$$E_{\text{repulsive}} = \frac{B}{r^n}$$

where B is a constant, *n* is of large value and depends upon electronic configuration.

Lennard – Jones Potential

The net energy of interactions is a sum of attractive and repulsive interactions. Lennerd–Jones proposed a model that combines the attractive and repulsive forces. It is given by

$$E_r = E_{\text{attractive}} + E_{\text{repulsive}} = \frac{A}{r^6} + \frac{B}{r^n}$$

where A and B are constants. The variation of Lennard–Jones potential with internuclear distance is given in Fig. 6.46.

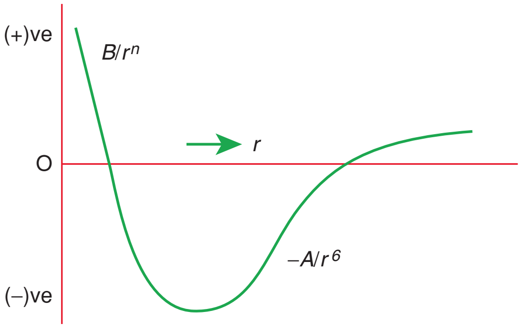


Figure 6.46 Plot of Lennard – Jones potential vs. internuclear distance.

6.20 | INTERACTIONS BETWEEN IONS AND COVALENT MOLECULES

The different types of interactions between ions and covalent molecules are listed as follows.

1. **Ion-dipole interactions:** These interactions are responsible for solubility of ionic compounds in polar solvents and are depicted in Fig. 6.47.

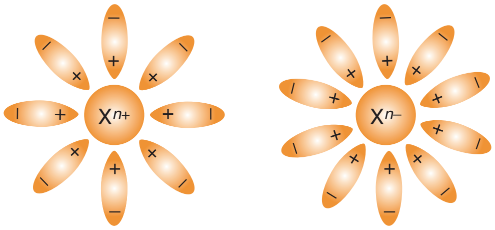


Figure 6.47 Ion-dipole interactions

2. **Ion-induced dipole interactions:** When an ion induces a dipole in a non-polar molecule, there is an electrostatic interaction between this ion and the induced dipole. The formation of polyhalide ion X_3^- (X = F, Cl, Br, I) is explained by these interaction as shown in Fig. 6.48.

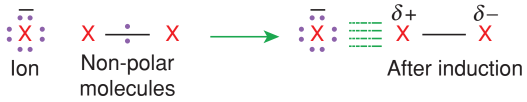


Figure 6.48 Ion-induced dipole interactions in formation of X_3^-

Note: Stability order for trihalide ions: $F_3^- < Cl_3^- < Br_3^- < I_3^-$. Since I^- is the largest ion and has the largest polarizibility. Hence, the donating ability of I^- is the maximum and I_3^- is most stable.

The interactions between ions and covalent molecules are determined by the inter-nuclear distance (r) and these decrease with increase in distance. The energy distance relationship between different types of interactions is given in Table 6.15.

Table 6.15 Energy distance function for different ion-covalent interactions

Type of interaction	Energy-distance function
Ion-dipole	$1/r^2$
Dipole-dipole (Keesom forces)	$1/r^3$
Ion-induced dipole	$1/r^4$
Dipole-induced dipole (Debye forces)	$1/r^6$
Instantaneous dipole-induced dipole (London forces)	$1/r^6$

SOLVED OBJECTIVE QUESTIONS FROM PREVIOUS YEAR PAPERS

1. According to MO theory, **(IIT-JEE 2004)**
   (A) O_2^+ is paramagnetic and bond order greater than O_2.
   (B) O_2^+ is paramagnetic and bond order less than O_2.
   (C) O_2^+ is diamagnetic and bond order less than O_2.
   (D) O_2^+ is diamagnetic and bond order more than O_2.

Solution

(A) The configuration of O_2 is $\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2$
$\sigma 2p_z^2 \pi 2p_x^2 = \pi 2p_y^2 \pi^* 2p_y^2$

Since it contains no unpaired electron, so O_2 is diamagnetic.

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{10-6}{2} = \frac{4}{2} = 2$$

The configuration of O_2^+ is $\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2$ $\sigma 2p_z^2 \pi 2p_x^2 = \pi 2p_y^2 \pi^* 2p_y^1$

Since it contains one unpaired electron, so O_2^+ are paramagnetic.

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{10-5}{2} = \frac{5}{2} = 2.5$$

Hence, bond order of O_2^+ is greater than O_2.

2. Among the following, the paramagnetic compound is

(A) Na_2O_2 (B) O_3

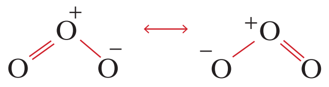
(C) N_2O (D) KO_2 **(IIT-JEE 2007)**

Solution

(D) In Na_2O_2, oxygen is present as peroxide, that is, O_2^{2-}. Considering molecular orbital theory for peroxide, we have

$$O_2^{2-} = \sigma 1s^2\ \sigma^* 1s^2\ \sigma 2s^2\ \sigma^* 2s^2\ \sigma 2p_z^2\ \pi 2p_x^2 = \pi 2p_y^2\ \pi^* 2p_x^2 = \pi^* 2p_y^2$$

We can see that there are no unpaired electrons. Considering the structure of O_3, there are no unpaired electrons



In N_2O, there are no unpaired electrons

$$N = N \rightarrow O$$

$$N_2O = \sigma 1s^2\ \sigma^* 1s^2\ \sigma 2s^2\ \sigma^* 2s^2\ \sigma 2p_z^2\ \pi 2p_x^2 = \pi 2p_y^2\ \pi^* 2p_x^2\ \sigma^* 2p_z^2\ \sigma 3s^2$$

In KO_2, oxygen is present as O_2^-, that is, superoxide. The molecular orbital theory for superoxide ion is

$$O_2^- = \sigma 1s^2\ \sigma^* 1s^2\ \sigma 2s^2\ \sigma^* 2s^2\ \sigma 2p_z^2\ \pi 2p_x^2 = \pi 2p_y^2\ \pi^* 2p_x^2 = \pi^* 2p_y^1$$

There is one unpaired electron in $\pi^* 2p_y$ orbital.

3. The species having bond order different from that in CO is

(A) NO^- (B) NO^+

(C) CN^- (D) N_2 **(IIT-JEE 2007)**

Solution

(A) NO^- is a 16 electron system (7 + 8 + 1 = 16) with zero bond order whereas the other molecules like CO, NO^+, CN^- and N_2 are 14 electron systems with bond order of 3.

4. Match each of the diatomic molecules in Column I with its property/properties in Column II. **(IIT-JEE 2009)**

Column I	Column II
(A) B_2	(p) Paramagnetic
(B) N_2	(q) Undergoes oxidation
(C) O_2^-	(r) Undergoes reduction
(D) O_2	(s) Bond order ≥ 2
	(t) Mixing of *s* and *p* orbitals

Solution

A → (p, r, t); B → (s, t); C → (p, q); D → (p, q, s)

(A) The electronic configuration B_2 is $\sigma 1s^2\ \sigma^* 1s^2\ \sigma 2s^2\ \sigma^* 2s^2\ \pi 2p_x^1 = \pi 2p_y^1$. Thus, it contains 2 unpaired electrons, undergoes reduction and there is mixing of *s* and *p* orbitals because they are equal in energies.

(B) The electronic configuration N_2 is $\sigma 1s^2\ \sigma^* 1s^2\ \sigma 2s^2\ \sigma^* 2s^2\ \pi 2p_x^2 = \pi 2p_y^2\ \sigma 2p_z^2$. Thus, the bond order is (10 – 4)/2 = 6/2 = 3. There is mixing of *s* and *p* orbitals because they are equal in energies.

(C) The electronic configuration O_2^- is $\sigma 1s^2\ \sigma^* 1s^2\ \sigma 2s^2\ \sigma^* 2s^2\ \sigma 2p_z^2\ \pi 2p_x^2 = \pi 2p_y^2\ \pi^* 2p_x^2\ \pi^* 2p_y^1$. Thus, it contains 1 unpaired electrons and undergoes oxidation.

(D) The electronic configuration O_2 is $\sigma 1s^2\ \sigma^* 1s^2\ \sigma 2s^2\ \sigma^* 2s^2\ \sigma 2p_z^2\ \pi 2p_x^2 = \pi 2p_y^2\ \pi^* 2p_x^1\ \pi^* 2p_y^1$. Thus, it contains 2 unpaired electrons and undergoes oxidation. Therefore, the bond order is (10 – 6)/2 = 4/2 = 2.

5. Using the data provided, calculate the multiple bond energy (kJ mol^{-1}) of a C

7. The species having pyramidal shape is

(A) SO_3 (B) BrF_3

(C) SiO_3^{2-} (D) OSF_2 **(IIT-JEE 2010)**

Solution

(D) OSF_2 has three bond pairs, one lone pair, with hybridization sp^3 and pyramidal geometry.

8. Based on VSEPR theory, the number of 90° F

Solution

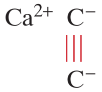
(B) In sp^3d^2 hybridization, the geometry is octahedral and all the bonds are at 90° to each other.

15. The number and type of bonds between two carbon atoms in calcium carbide are **(AIEEE 2005)**

(A) One sigma, one pi
(B) One sigma, two pi
(C) Two sigma, one pi
(D) Two sigma, two pi

Solution

(B) CaC_2 contains one sigma and two pi bonds.

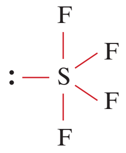


16. The molecular shapes of SF_4, CF_4 and XeF_4 are **(AIEEE 2005)**

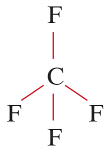
(A) the same with 2, 0 and 1 lone pairs of electrons.
(B) the same with 1, 1 and 1 lone pair of electrons on the central atoms, respectively.
(C) different with 0, 1 and 2 lone pairs of electrons on the central atom, respectively.
(D) different with 1, 0 and 2 lone pairs of electrons on the central atom, respectively.

Solution

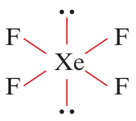
(D) The structures are as follows:



SF_4
See-saw
1 lone pair



CF_4
Tetrahedral
0 lone pair



XeF_4
Square planar
2 lone pairs

17. Lattice energy of an ionic compound depends upon **(AIEEE 2005)**

(A) charge on the ion only.
(B) size of the ion only.
(C) packing of ions only.
(D) charge on the ion and size of the ion.

Solution

(D) This is because it involves both the attractive forces between ions of opposite charges and the repulsive forces between ions of like charges.

18. Which one of the following species is diamagnetic in nature? **(AIEEE 2005)**

(A) He_2^+
(B) H_2
(C) H_2^+
(D) H_2^-

Solution

(B) According to MO theory, configuration of H_2 is $\sigma 1s^2\ \sigma^*1s^2$. There are no unpaired electrons, so it is diamagnetic.

19. The bond order in NO is 2.5 whereas that in NO^+ is 3. Which of the following statements is true for these two species? **(AIEEE 2004)**

(A) Bond length in NO^+ is greater than in NO
(B) Bond length is unpredictable
(C) Bond length in NO^+ in equal to that in NO
(D) Bond length in NO is greater than in NO^+

Solution

(D) Bond length in NO is greater than in NO^+. As we know that the bond order is inversely proportional to the bond length. So, greater is the bond order and shorter is the bond length.

20. The states of hybridization of boron and oxygen atoms in boric acid (H_3BO_3) are, respectively,

(A) sp^2 and sp^2
(B) sp^3 and sp^3
(C) sp^3 and sp^2
(D) sp^2 and sp^3

(AIEEE 2004)

Solution

(D) Ground state configuration of boron is

$$1s^2\, 2s^1\, 2p_x^1\, 2p_y^1$$

Excited state configuration is $1s^2\ 2s^1\ 2p_x^1\ 2p_y^1$.

This means that boron atom undergoes sp^2 hybridization and each of these three sp^2 orbitals overlap with 2p orbitals of O^- ion to form three BO^- bonds.

21. Which one of the following has the regular tetrahedral structure? **(AIEEE 2004)**

(A) XeF_4
(B) $[Ni(CN)_4]^{2-}$
(C) BF_4^-
(D) SF_4

Solution

(C) The expression is

$$\text{Hybridization} = \frac{(V + M - c + a)}{2}$$

where V is the number of valence electrons of the metal, M is the number of monovalent atoms attached, c is the charge on cation and a is the charge on anion, we get

$$\text{Hybridization of } BF_4^- = \frac{(3+4-0+1)}{2} = \frac{8}{2} = 4$$

Therefore, the hybridization is sp^3.

22. Which of the following molecules/ions does not contain unpaired electrons? **(AIEEE 2006)**

(A) O_2^{2-}
(B) B_2
(C) N_2^+
(D) O_2

Solution

(A) The bond order of O_2^{2-} is $\sigma 1s^2\, \sigma^*1s^2\, \sigma 2s^2\, \sigma^*2s^2$ $\sigma 2p_z^2\, \pi 2p_x^2 = \pi 2p_y^2\, \pi^*2p_x^2 = \pi^*2p_y^2$.

Hence, there are no unpaired electrons.

The bond order of B_2 is $\sigma 1s^2\, \sigma^*1s^2\, \sigma 2s^2\, \sigma^*2s^2\, \pi 2p_x^1 = \pi 2p_y^1$.

Hence, there are two unpaired electrons.

The bond order of N_2^+ is $\sigma 1s^2 \sigma * 1s^2 \sigma 2s^2 \sigma * 2s^2 \pi 2p_x^2 = \pi 2p_y^2\ \sigma 2p_z^1$.

Hence, there is one unpaired electron.

The bond order of O_2 is $\sigma 1s^2 \sigma * 1s^2 \sigma 2s^2 \sigma * 2s^2 \sigma 2p_z^2 = \pi 2p_y^2 \pi * 2p_x^1 = \pi * 2p_y^1$.

Hence, there are two unpaired electrons.

23. In which of the following molecules/ions are all the bonds not equal? **(AIEEE 2006)**

(A) SF_4
(B) SiF_4
(C) XeF_4
(D) BF_4^-

Solution

(A) S has 6 valence electrons. However, in SF_4 there are 4 bonds, so 4 of the valence electrons from S are used in bonding. Since 2 of them are not involved in bonding, they exist as a lone pair. SF_4 is based on trigonal bipyramidal structure. The lone pair present will repel the 4 bond pairs, thereby distorting the trigonal bipyramidal shape and leading to non-equal bonds.

24. Which of the following species exhibits the diamagnetic behavior?

(A) NO
(B) O_2^{2-}
(C) O_2^+
(D) O_2 **(AIEEE 2007)**

Solution

(B) The electronic configurations are as follows:

$$O_2^{2-} = \sigma 1s^2\ \sigma * 1s^2\ \sigma 2s^2\ \sigma * 2s^2\ \sigma 2p_z^2\ \pi 2p_x^2 = \pi 2p_y^2\ \pi * 2p_x^2 = \pi * 2p_y^2$$

There is no unpaired electron, so it is diamagnetic.

$$O_2^+ = \sigma 1s^2\ \sigma * 1s^2\ \sigma 2s^2\ \sigma * 2s^2\ \sigma 2p_z^2\ \pi 2p_x^2 = \pi 2p_y^2\ \pi * 2p_x^1$$

There is one unpaired electron, so it is paramagnetic.

$$O_2 = \sigma 1s^2\ \sigma * 1s^2\ \sigma 2s^2\ \sigma * 2s^2\ \sigma 2p_z^2\ \pi 2p_x^2 = \pi 2p_y^2\ \pi * 2p_x^1 = \pi * 2p_y^1$$

There are two unpaired electrons, so it is paramagnetic. NO is isoelectronic with O_2^+, so it also has one unpaired electron, and is paramagnetic.

25. In which of the following ionization processes, the bond order has increased and the magnetic behavior has changed? **(AIEEE 2007)**

(A) $N_2 \to N_2^+$
(B) $C_2 \to C_2^+$
(C) $NO \to NO^+$
(D) $O_2 \to O_2^+$

Solution

(C) The electronic configurations are

$$C_2 = \sigma 1s^2\ \sigma * 1s^2\ \sigma 2s^2 \sigma * 2s^2\ \pi 2p_x^2 = \pi 2p_y^2$$

$$C_2^+ = \sigma 1s^2\ \sigma * 1s^2\ \sigma 2s^2\ \sigma * 2s^2\ \pi 2p_x^2 = \pi 2p_y^1$$

The election has been removed from bonding molecular orbital, so the bond order decreases.

In $NO \to NO^+$

$$NO = \sigma 1s^2\ \sigma * 1s^2\ \sigma 2s^2 \sigma * 2s^2\ \sigma 2p_z^2\ \pi 2p_x^2 = \pi 2p_y^2\ \pi * 2p_x^1 = \pi 2p_y^0$$

$$NO^+ = \sigma 1s^2\ \sigma * 1s^2\ \sigma 2s^2 \sigma * 2s^2\ \sigma 2p_z^2\ \pi 2p_x^2 = \pi 2p_y^2$$

The electron has been removed from antibonding orbital, so bond order increases and nature changes from paramagnetic to diamagnetic.

26. The charge/size ratio of a cation determines its polarizing power. Which one of the following sequences represents the increasing order of the polarizing power of the cationic species, K^+, Ca^{2+}, Mg^{2+} and Be^{2+}? **(AIEEE 2007)**

(A) $Ca^{2+} < Mg^{2+} < Be^{2+} < K^+$

(B) $Mg^{2+} < Be^{2+} < K^+ < Ca^{2+}$

(C) $Be^{2+} < K^+ < Ca^{2+} < Mg^{2+}$

(D) $K^+ < Ca^{2+} < Mg^{2+} < Be^{2+}$

Solution

(D) Higher is the charge/size ratio, higher is the polarizing power.

27. Which of the following hydrogen bonds is the strongest? **(AIEEE 2008)**

(A) O

The molecular orbital configuration of O_2^{2-} is

$$\sigma 1s^2\ \sigma^* 1s^2\ \sigma 2s^2\ \sigma^* 2s^2\ \sigma 2p_z^2\ \pi 2p_x^2 = \pi 2p_y^2\ \pi^* 2p_x^2 = \pi^* 2p_y^2$$

Bond order of $O_2^{2-} = (1/2)\ (10 - 8) = 1$.

The molecular orbital configuration of O_2^{2+} is

$$\sigma 1s^2\ \sigma^* 1s^2\ \sigma 2s^2\ \sigma^* 2s^2\ \sigma 2p_z^2\ \pi 2p_x^2 = \pi 2p_y^2$$

Bond order of $O_2^{2+} = (1/2)\ (10 - 4) = 3$.

The molecular orbital configuration of O_2^{+} is

$$\sigma 1s^2\ \sigma^* 1s^2\ \sigma 2s^2\ \sigma^* 2s^2\ \sigma 2p_z^2\ \pi 2p_x^2 = \pi 2p_y^2\ \pi^* 2p_x^1$$

Bond order of $O_2^{+} = (1/2)\ (10 - 5) = 2.5$.

Out of these, O_2^{2+} has the highest bond order, so the lowest bond length as bond length is inversely proportional to bond order.

30. The bond dissociation energy of B

35. Stability of the species Li_2, Li_2^- and Li_2^+ increases in the order of

(A) $Li_2^- < Li_2^+ < Li_2$ (B) $Li_2 < Li_2^- < Li_2^+$

(C) $Li_2^- < Li_2 < Li_2^+$ (D) $Li_2 < Li_2^+ < Li_2^-$

(JEE Main 2013)

Solution

(A) Bond order = $\frac{1}{2}$ (bonding electrons – antibonding electrons) ; Stability $\propto$ B.O.

$$Li_2 (\text{atomic number} = 6) = \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2;$$

$$\text{Bond order} = \frac{4-2}{2} = 1$$

$$Li_2^+ (\text{atomic number} = 6) = \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^1;$$

$$\text{Bond order} = \frac{3-2}{2} = 0.5$$

$$Li_2^- (\text{atomic number} = 7) = \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^1;$$

$$\text{Bond order} = \frac{4-3}{2} = 0.5$$

Li_2^+ is more stable than Li_2^- because bond order of Li_2^- is less than that of Li_2^+.

Hence, the order is $Li_2^- < Li_2^+ < Li_2$.

36. Which one of the following molecules is expected to exhibit diamagnetic behaviour?

(A) N_2 (B) O_2

(C) S_2 (D) C_2

(JEE Main 2013)

Solution

(A), (D)

$$N_2 = \sigma 1s^2 \sigma^* 1s^2, \sigma 2s^2 \sigma^* 2s^2, \left\{\begin{matrix}\pi 2p_y{}^2 \\ \pi 2p_z^2\end{matrix}\right. \quad \sigma 2p_x{}^2$$

$$O_2 = \sigma 1s^2 \sigma^* 1s^2, \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_x, \left\{\begin{matrix}\pi 2p_y{}^2 \\ \pi 2p_z{}^2\end{matrix}\right. \left\{\begin{matrix}\pi^* 2p_y{}^1 \\ \pi^* 2p_z{}^1\end{matrix}\right.$$

$$C_2 = \sigma 1s^2 \sigma^* 1s^2,\ \sigma 2s^2 \sigma^* 2s^2 \left\{\begin{matrix}\pi 2p_y{}^2 \\ \pi 2p_z{}^2\end{matrix}\right.$$

N_2 and C_2 exhibit diamagnetic behaviour as they do not possess unpaired electrons, while O_2 and S_2 exhibit paramagnetic behaviour due to the presence of all the paired electrons.

37. In which of the following pairs of molecules/ions, both the species are not likely to exist?

(A) H_2^-, He_2^{2-} (B) H_2^{2+}, He_2

(C) H_2^-, He_2^{2+} (D) H_2^+, He_2^{2-}

(JEE Main 2013)

Solution

The bond order of various species

(A)

$H_2^- = \frac{1}{2}[3-1] = 0.5$ exist

$He_2^{2-} = \frac{1}{2}[2-2] = 0$ not exist

(2)

$H_2^{2+} = \frac{1}{2}[0-0] = 0$ not exist

$He_2 = \frac{1}{2}[2-2] = 0$ not exist

(C)

$H_2^- = \frac{1}{2}[2-1] = 0.5$ exist

$He_2^{2+} = \frac{1}{2}[2-0] = 1$ exist

(D)

$H_2^+ = \frac{1}{2}[1-0] = 0.5$ exist

$He_2^{2-} = \frac{1}{2}[2-2] = 0$ not exist

Bond order of H_2^{2+} and He_2 is zero, thus their existence is not possible.

38. Which one of the following properties is not shown by NO?

(A) It is diamagnetic in gaseous state.

(B) It is a neutral oxide.

(C) It combines with oxygen to form nitrogen dioxide.

(D) Its bond order is 2.5.

(JEE Main 2014)

Solution

(A) The MO configuration of NO is

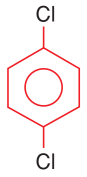
$$\sigma 1s^2\ \sigma^* 1s^2 \sigma 2s^2\ \sigma^* 2s^2 \sigma 2p_z^2\ \pi 2p_x^2\ \pi 2p_y^2\ \pi^* 2p_x^1$$

As can be seen it is an odd electron species and so paramagnetic in gaseous state with one unpaired electron.

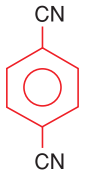
Bond order = (10 – 5)/2 = 2.5.

39. For which of the following molecule significant $\mu \neq 0$?

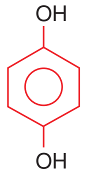
(a)



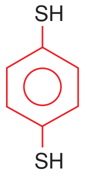
(b)



(c)



(d)



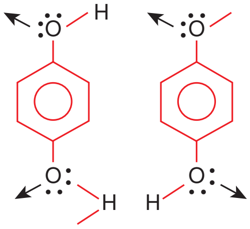
(A) Only (a) (B) (a) and (b)

(C) Only (c) (D) (c) and (d)

(JEE Main 2014)

Solution

(D) In (a) and (b), $\mu = 0$ as the dipole moments cancel each other. However, in (c) and (d) more than one conformation is possible, so, the dipole moment is not zero in those cases. For example, possible conformations in (c) are shown below.



Similarly for structure (d), two conformations are possible.

40. The intermolecular interaction that is dependent on the inverse cube of distance between the molecules is:

(A) ion-dipole interaction
(B) London force
(C) hydrogen bond
(D) ion-ion interaction

(JEE Main 2015)

Solution

(C) Hydrogen bond is a special case of dipole–dipole interaction, so for stationary polar molecules,

$$F \propto \frac{1}{r^3}$$

REVIEW QUESTIONS

1. In the CO_2 molecule, where are the non-bonding electrons? How many electrons are in bonding domains?

2. Which sets are pairs of resonance contributing structures?

3. Which of the following molecules have resonance structures?

(a) HCN **(b)** SO_2 **(c)** PCl_3 **(d)** OCN^-

4. A possible Lewis structure for CO_2 involves a triple bond and a single bond between C and the O’s. Write the two resonance structures involving the triple bond. What is implied about the nature of the C

27. (A) Are all dissymmetric molecules polar?
(B) What condition must be met if a molecule having polar bonds is to be non-polar?

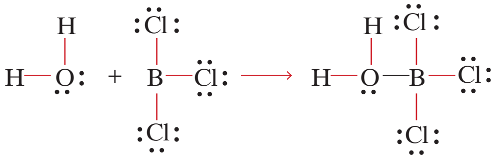
28. Why do elements of the second period never use sp^3d or sp^3d^2 hybrid orbitals for bond formation?

29. What relationship is there, if any, between Lewis structures and the valence bond descriptions of molecules?

30. How can the VSEPR model be used to predict the hybridization of an atom in a molecule?

31. If the central oxygen in the water molecule did not use sp^3 hybridized orbitals (or orbitals of any other kind of hybridization), what would be the expected bond angle in H_2O (assuming no angle-spreading force)?

32. How does the geometry around B and O change in the following reaction? How does the hybridization of each atom change?



33. On the basis of MO theory, explain why Li_2 molecules can exist but Be_2 molecules cannot. Could the ion Be_2^+ exist?

34. Use sketches of orbitals to describe how valence bond theory would explain the formation of H

ADDITIONAL OBJECTIVE QUESTIONS

Single Correct Choice Type

1. Structure of IF_4^+ and hybridization of iodine in this structure is, respectively,
(A) linear, sp^3d
(B) K-shaped, sp^3d^2
(C) irregular tetrahedral, sp^3d
(D) square planar, sp^3d^2

2. Which of the following is/are not correct regarding C_2 molecule?
(A) C_2 molecule has been found to exist in vapor phase.
(B) It has a total 12 electrons, out of which 8 electrons occupy bonding orbitals while 4 electrons occupy antibonding orbitals.
(C) The molecule is paramagnetic.
(D) C_2 molecule contains double bond and both are π bonds.

3. What fraction of charge is present on iodine in covalently bonded $H^{\delta+}-I^{\delta-}$. If the dipole moment of HI is 0.38 D and the bond length is 1.61 Å.
(A) 5%
(B) 16%
(C) 33%
(D) 79%

4. The correct order for the bond angles of NO_2, NO_2^+, NO_2^- and NO_3^- is
(A) $NO_2^+ > NO_3^- > NO_2^- > NO_2$
(B) $NO_2^+ > NO_2 > NO_3^- > NO_2^-$
(C) $NO_3^- > NO_2 > NO_2^+ > NO_2^-$
(D) $\overset{+}{N}O_2 > NO_2^- > NO_3^- > NO_2$

5. Which of the following molecules is/are having zero dipole moment
(I) PCl_3Br_2 (stable isomer)
(II) XeF_4
(III) SF_6
(IV) ClF_3
(A) only II, IV
(B) only I, II
(C) only I, II, III
(D) only III, IV

6. Bond order of O_2, O_2^+, O_2^- and O_2^{2-} is in order:
(A) $O_2^- < O_2^{2-} < O_2 < O_2^+$
(B) $O_2^{2-} < O_2^- < O_2 < O_2^+$
(C) $O_2^+ < O_2 < O_2^- < O_2^{2-}$
(D) $O_2 < O_2^+ < O_2^- < O_2^{2-}$

7. The number of σ and π bonds in tetravalent perxenate anion is
(A) 6σ and 1π
(B) 6σ and 2π
(C) 4σ and 4π
(D) 4σ and 6π

8. Which of the following can be calculated from the Born–Haber cycle of formation of Al_2O_3?
(A) Lattice enthalpy of Al_2O_3.
(B) Electron gain enthalpy of O atom.
(C) Hydration enthalpy of Al^{3+}.
(D) Ionization enthalpy of Al.

9. The correct order of increasing C–O bond strength of CO, CO_3^{2-}, CO_2 is:
(A) $CO_3^{2-} < CO_2 < CO$
(B) $CO_2 < CO_3^{2-} < CO$
(C) $CO < CO_3^{2-} < CO_2$
(D) $CO < CO_2 < CO_3^{2-}$

10. Hybridization, shape and number of π bonds in $XeOF_2$ molecule are, respectively,
(A) sp^3, pyramidal, 1
(B) sp^3d, trigonal bipyramidal, 2
(C) sp^3d, T-shaped, 1
(D) sp^3d, square pyramidal, 1

11. Carbon dioxide is isostructural with
(A) $HgCl_2$
(B) $SnCl_2$
(C) C_2H_4
(D) NO_2^-

12. Select the incorrect statement among the following:
(A) NF_3 is weaker base then NH_3.
(B) $AlCl_3$ is largely covalent while AlF_3 is largely ionic.
(C) $B_2H_6{\cdot}2NH_3$ is ionic.
(D) NO has one unpaired electron in bonding molecular orbital.

13. The correct order of dipole moment is
(A) $CH_4 < NF_3 < NH_3 < H_2O$
(B) $NF_3 < CH_4 < NH_3 < H_2O$
(C) $NH_3 < NF_3 < CH_4 < H_2O$
(D) $H_2O < NH_3 < NF_3 < CH_4$

14. Element A has three electrons in the outermost orbit and B has six electrons in the outermost orbit. The formula of the compound will be
(A) A_2B_3
(B) A_2B_6
(C) A_2B
(D) A_3B_2

15. Polarization of ions is governed by
(A) hybridization.
(B) VSEPR theory.
(C) Fajans' rules.
(D) Pauling's rule.

16. The pair of elements from ionic bond is
(A) C + Cl
(B) H + F
(C) Na + Br
(D) O + H

17. The correct order of decreasing polarizable ions is
(A) Cl^-, Br^-, I^-, F^-
(B) F^-, I^-, Br^-, Cl^-
(C) F^- Cl^-, Br^-, I^-
(D) I^- Br^-, Cl^-, F^-

18. The bond present in N_2O_5 is
(A) only ionic.
(B) covalent and coordinate.
(C) only covalent.
(D) covalent and ionic.

19. Which of these contain both polar and non-polar bonds?
(A) HCN
(B) CO_2
(C) H_2O_2
(D) CH_4

20. Paramagnetism is observed in
(A) N_2
(B) O_2
(C) He
(D) O_2^{2-}

21. Which of the following species has the shortest bond length?
(A) NO^{2+}
(B) NO^+
(C) NO
(D) NO^-

22. Among the following, which is polar?

(A) CO_2 (B) SO_2

(C) $BeCl_2$ (D) Cl

(B) When BF_3 is added to Na_3AlF_6, Na_3BF_4 is formed.
(C) All alkaline earths form peroxides on heating in excess of oxygen.
(D) Magnesium cannot be extracted by the electrolysis of fused $Mg(OH)_2$.

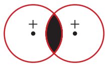
5. Which among the following species have zero bond order?

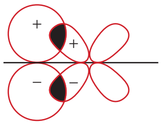
(A) F_2^{2-}
(B) Ar_2
(C) He_2^+
(D) H_2^+

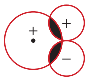
6. Which of the following molecules are polar and sp^3d^2 hybridized?

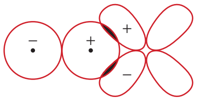
(A) IF_5
(B) XeF_4
(C) $XeOF_4$
(D) ICl_4^-

7. Which of the following combination(s) of atomic orbitals suggest non-bonding combinations of atomic orbitals?

(A)


(B)


(C)


(D)


8. Correct order about bond angle is

(A) $H_2O > H_2S > H_2Se > H_2Te$
(B) $C_2H_2 > C_2H_4 > CH_4 > NH_3$
(C) $SF_6 < NH_3 < H_2O < OF_2$
(D) $ClO_2 > H_2O > H_2S > SF_6$

9. Which of following energy terms are associated with the Born–Haber cycle of dissociation of $BaCl_2$ in water?

(A) Hydration enthalpy of Ba^{2+}.
(B) Lattice enthalpy of $BaCl_2$.
(C) Sublimation enthalpy of Ba.
(D) Electron gain enthalpy of Cl^-.

10. In which of the following, the hybrid orbitals of the central atom have the same *s* character?

(A) CH_4
(B) $Ni(CO)_4$
(C) XeO_3
(D) $[Ni(CN)_4]^{2-}$

11. Which of the following set correctly represent sp^3 hybridization and tetrahedral geometry?

(A) ClO_4^-, SO_4^{2-}, Diamond
(B) SiO_4^{4-}, $[PCl_4]^-$, SiC
(C) $Ni(CO)_4$, $SnCl_4$, Graphite
(D) Ice, $FClO_3$, $[Zn(H_2O)_4]^{-2}$

12. Among the following bonds, which are more ionic than covalent?

(A) Si

Comprehension Type

Read the paragraphs and answer the questions that follow:

Paragraph I

The following steps help predict the geometrical shape of species with only one central atom, without first drawing the Lewis structure:

(a) Total number of σ electron pairs = (number of valence electrons ± electrons (for ionic charges)/2

(b) Number of bonded electron pairs = number of atoms – 1

(c) Number of electron pairs around central atom = total number of electron pairs – 3 [number of terminal atoms (except H)]

(d) Number of lone pairs = (number of central electron pairs – number of bond pairs)

1. Based on above method, structure of the some of the molecules have been matched. Which is the incorrect matching?

(A) ICl_2^- – Linear
(B) ClO_3^- – Pyramidal
(C) ICl_4^- – Square planar
(D) $PdCl_4^{-2}$ – Tetrahedral

2. If A is the central element of the molecule containing A and X elements and *L* is the number of lone pairs around it, then VSEPR notation AX_3L will be for the molecules:

(A) PCl_3, ICl_4^-
(B) NH_3, H_2O
(C) NH_3, ClO_3^-
(D) ICl_4^- , ClO_3^-

3. Square planar structure is predicated for:

(A) ICl_4^- , ClO_3^-
(B) XeF_4, XeO_4
(C) BrF_5, Al_2Cl_6
(D) ICl_4^- , $PtCl_4^{-2}$

Paragraph II

Valence shell electron repulsion theory (VSEPR) can be used to predict the approximate shape of a molecule. Electrons in bonds and in lone pairs can be thought of as “charge cloud” that repel one another and stay as far apart possible, thus causing molecules to assume specific shapes.

The repulsive interactions of electron pairs decrease in the order:

Lone pair–lone pair > Lone pair–bond pair > Bond pair–bond pair.

These repulsions effect result in deviations from idealized shapes and alteration in bond angles in molecules.

4. Molecular shape of XeF_3^+, SF_3^+ and CF_3^+ are

(A) the same with 2, 1 and 0 lone pairs of electrons, respectively.
(B) different with 2, 1 and 0 lone pairs of electrons, respectively.
(C) different with 0, 1 and 2 lone pairs of electrons, respectively.
(D) the same with 2, 0 and 1 lone pairs of electrons, respectively.

5. Which of the following statements is correct with respect to bond angle?

(A) The F

(B) N

4. Match the molecules/species with the properties.

Column I	Column II
(A) BrF_5	(p) It has atleast one angle less than 90°.
(B) ICl_3	(q) The central atom is sp^3d hybridized.
(C) H_3O^+	(r) It is non-planar.
	(s) The central atom is having only one lone pair.

5. Match the hybrid bond orbitals with the species.

Column I	Column II
(A) sp^3	(p) AsF_6^-
(B) dsp^2	(q) $TeCl_4$
(C) sp^3d	(r) SiO_2
(D) sp^3d^2	(s) $[Ni(en)_2]^+$

ANSWERS

Review Questions

1. The non-bonding electrons are located in the non-bonding electron domains of the oxygen atoms. There are four electrons present in the bonding domains between carbon and oxygen.

2. Pair (a) is a set of resonance structures.

3. (b) and (d)

5. Band theory

13. Linear structure

14. sp^3

15. Two unpaired electrons

19. Noble gases

20. Ten

25. **(a)** Trigonal planar; **(c)** octahedral;
(b) tetrahedral; **(d)** trigonal bipyramidal

28. Elements in the second period do not have a *d* subshell in the valence level.

31. 90°

35. Iodine heptaflouride has sp^3d^3 hybridization.

36. **(a)** sp^2; **(b)** sp; **(c)** sp^3;
(d) sp^2; **(e)** $sp^{3;}$

37. Hydrogen bonding

Numerical Problems

1. 1.24 D

2. On the sodium the charge is $+0.795\ e^-$ and on the chlorine, the charge is $-0.795\ e^-$. This would be 79.5% positive charge on the Na and 79.5% negative charge on the Cl.

3. 20.56%

4. The formal charges on the atoms in HCl are 0. The actual charges are H: $+0.17e^-$ and Cl: $-0.17e^-$

5. 30 times.

6. The lattice energy for NaCl is 787 kJ. The large difference in lattice energy is a result of charge (divalent versus univalent) and size of ions.

7. Br

8. 72.24%

9. N = 0; O = 0 and O = –1

10. $-2870.8\ \text{kJ mol}^{-1}$.

11. 16.83%

Additional Objective Questions

Single Correct Choice Type

1. (C)
2. (C)
3. (A)
4. (B)
5. (C)
6. (B)
7. (B)
8. (A)
9. (A)
10. (C)
11. (A)
12. (D)
13. (A)
14. (A)
15. (C)
16. (C)
17. (A)
18. (B)
19. (C)
20. (B)
21. (B)
22. (B)
23. (C)
24. (D)
25. (B)
26. (A)
27. (A)
28. (D)
29. (C)
30. (A)
31. (C)
32. (D)
33. (B)
34. (B)
35. (A)
36. (C)
37. (C)
38. (B)
39. (D)
40. (B)
41. (A)
42. (D)

Multiple Correct Choice Type

1. (A, B, C)
2. (A, D)
3. (A, C)
4. (A, B, D)
5. (A, B)
6. (A, C)
7. (C, D)
8. (A, B, D)
9. (A, B)
10. (A, C)
11. (A, B, D)
12. (B, D)
13. (A, C, D)

Assertion–Reasoning Type

1. (A)
2. (B)
3. (B)
4. (D)
5. (C)
6. (A)
7. (C)
8. (D)
9. (A)
10. (C)
11. (D)

Comprehension Type

1. (D)
2. (C)
3. (D)
4. (B)
5. (C)
6. (D)
7. (D)
8. (B)
9. (B)
10. (A)
11. (D)
12. (C)
13. (C)
14. (C)
15. (A)
16. (B)
17. (C)

Integer Answer Type

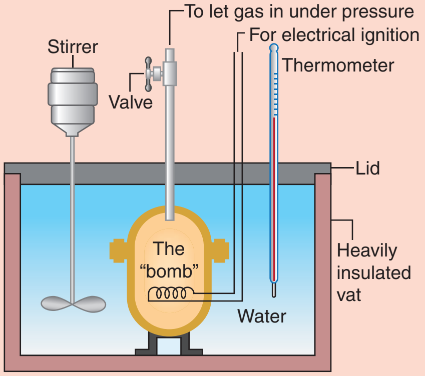
1. (4)
2. (7)
3. (0)
4. (6)
5. (4)
6. (+9)
7. (2)
8. (4)

Matrix–Match Type

1. A → (q, r); B → (p, s); C → (p, s); D → (q, r)
2. A → (p); B → (q); C → (p); D → (s)
3. A → (p, q); B → (p, q, r); C → (p, q, r, s); D → (p, q, r, s)
4. A → (s); B → (p, s); C → (q, r); D → (q, r)
5. A → (r); B → (s); C → (q); D → (p)

7

Chemical Energetics



A bomb calorimeter

Contents

7.1 Fundamentals of Thermodynamics
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7.3 Energy of the Thermodynamic System
7.4 The First Law of Thermodynamics
7.5 Calculation of Work in Different Processes
7.6 Enthalpy or Heat Content, *H*
7.7 Expansion and Compression of an Ideal gas
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7.9 Calorimetry
7.10 Thermochemistry
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7.12 Laws of Thermochemistry
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The study of flow of heat in or out of a system during its physical or chemical transformation is known as **thermodynamics**. Any other form of energy brings about changes in certain properties of the system, such as temperature, pressure, volume and concentration of the system. The changes in these quantities from initial to final state of the system can be measured. They provide information regarding energy changes and accompanying changes in related quantities like heat and work.

The study of thermodynamics is based on three broad generalizations known as the first, second and third laws of thermodynamics. Based on these laws, thermodynamics helps us determine the following:

1. Derivation of quantitative relations between heat and other forms of energy.
2. Derivation of various laws, such as law of mass action, etc., thermodynamically.
3. Criteria for predicting the feasibility of change (physical and chemical).
4. Extent of change before equilibrium is reached, thus finding out the equilibrium conditions.
5. Efficiency of various types of engines.

The study of thermodynamics, however, has the following two limitations:

1. It only tells us about the initial and final states of the system. It is not concerned about the rate of the associated physical or chemical reaction.
2. It is applicable only to macroscopic systems and does not apply to microscopic systems of individual atoms or molecules.

7.1 | FUNDAMENTALS OF THERMODYNAMICS

Some important terms related to thermodynamics are as follows.

System and its Surroundings

1. **System:** It is any region of space that is under thermodynamic investigation.
2. **Surrounding:** It comprises the rest of the universe apart from the system (Fig. 7.1). Usually, the region in space in the neighborhood of the system constitutes the surroundings.
3. **Universe:** It comprises the system and the surroundings together.
4. **Boundary:** A wall or layer separating the system from the surroundings is called boundary. It can be visible (like the walls of a beaker) or invisible (like the Cartesian coordinates specifying a particular volume in space). Defining a boundary helps us control and track the changes in matter and energy between the system and the surroundings. A boundary may be classified into any of the following types:
   - **(a)** Real or imaginary boundary: If a physical wall or layer separating the system and surrounding is present, it is called a real boundary (e.g., the walls of the closed room). If an invisible separation between system and surrounding is present, it is called an imaginary boundary (e.g., an open beaker where beaker is the system).
   - **(b)** Rigid or flexible boundary: If the boundary has a fixed dimension then it is rigid. If the boundary has dimensions which can be changed, then it is flexible boundary. For example, boundary of a room will be rigid boundary whereas boundary of a balloon will be flexible.
   - **(c)** Dithermal or adiabatic boundary: A boundary which allows heat to flow through it is dithermal whereas a boundary which does not allow heat to flow through it is adiabatic. For example, a thermos flask (completely insulated) is an example of adiabatic boundary and a metal container is example of a dithermal boundary.

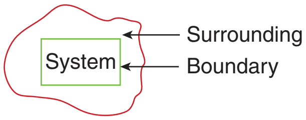


Figure 7.1 Schematic representation of a thermodynamic system.

For example, if we want to measure some physical properties of water, such as temperature or density, we place water in a beaker. Then the beaker containing water constitutes the system, and the remaining part of the universe. In this case, the room in which the beaker is kept, is the surroundings.

Types of the System

Depending on the movement of matter and energy, the system can be of the following types:

1. **Open system:** In such a system, matter can be added or removed from the system, since the boundary is open. The system is also not insulated. In such a system, both energy and matter can be transferred to and from the surroundings [Fig. 7.2(a)]. For example, hot water tumbler placed on a table. In this case, an imaginary surface surrounding the tumbler containing water and the air around will form the boundary of the system.
2. **Closed system:** In such a system, matter can neither be added nor removed, since the boundary of the system is sealed. The system is however, not insulated. In such a system, matter cannot be transferred but energy can be transformed in the form of heat or work to and from the surroundings [Fig. 7.2(b)]. For example, gas contained in a cylinder fitted with a piston or reactants present in a closed flask made of copper or any other conducting material.
3. **Isolated system:** In such a system, neither energy nor matter can be transferred to or from the surroundings, since the boundary is both sealed and insulated. Such a system has no interaction with the surroundings [Fig. 7.2(c)]. For example, boiling water contained in a thermos flask.

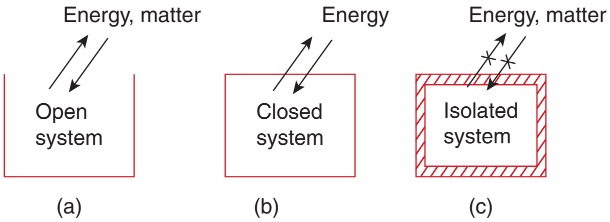


Figure 7.2 (a) Open system, (b) closed system and (c) isolated system.

Note: An open system will have an imaginary, flexible and dithermal boundary. Closed system will have real, rigid and dithermal boundary. An isolated system will have real, rigid and adiabatic boundary. Unless mentioned otherwise, assume the system to be a closed system.

Thermodynamic Properties

1. **Macroscopic properties:** These are properties of system related to a large number of molecules of system, that is, to the bulk of the system. Macroscopic properties of system are always related by an equation of state. For example, $pV = nRT$ is an equation of state by gas. Examples of macroscopic properties are pressure, volume, mass, temperature, number of moles, density, etc.
2. **Intensive properties:** These are properties which are independent of the quantity of matter present in the system. For example, temperature, pressure, density, concentration, etc. If a glass of water (system under consideration) is divided into two equal or unequal parts, then both the parts will have the same temperature, independent of the quantity of material present.

$$\text{Intensive property} \propto n^0$$

where, n is the number of moles. Examples of intensive properties are pressure, temperature, density, concentration terms, pH, specific heat, molar heat capacity, molar entropy, molar enthalpy, molar internal energy, boiling point, melting point, color.

3. **Extensive properties:** These are properties that depend on the quantity of matter present in the system. For example, volume, number of moles, entropy, Gibbs free energy, enthalpy, etc. These properties are additive, while intensive properties are not. If a glass of water (system under consideration) is divided into two equal parts, then both the parts will have same temperature, independent of the quantity of material present, however, the volume of water in each glass will be halved. Thus, temperature is an intensive property while volume is an extensive property. A molar property of an extensive property is intensive. To understand this, let us consider any extensive property of a system, say χ, then the value for the molar property would be

$$\chi_{\mathrm{m}} = \frac{\chi}{n}$$

where n is the number of moles; χ_{m} is then an intensive property independent of the amount of matter. Other extensive properties such as volume, heat capacity, etc. can be expressed as molar values V_{m} and C_{m}, which are intensive properties.

$$\text{Extensive property} \propto n^1.$$

Examples of extensive properties are mass, volume, moles, internal energy, enthalpy, entropy, Gibbs free energy, heat capacity.

Note: If I = intensive property and E = extensive property, then

$\frac{I}{I} \propto n^\circ$, therefore, $\frac{I}{I}$ is an extensive property.

$\frac{E}{E} \propto \frac{n^1}{n^1} = n^\circ$, therefore, $\frac{E}{E}$ is an intensive property.

$\frac{I}{E} \propto \frac{n^\circ}{n^1} = n^{-1}$, therefore, it can either be intensive or extensive property.

$\frac{E}{I} \propto \frac{n^1}{n^\circ} = n^1$, therefore, $\frac{E}{I}$ is an extensive property.

4. **State of the system:** These set of variables, such as temperature, pressure, composition, etc., that describe the system is known as the state of the system. If any of these variables undergo a change, the system is said to undergo change of state.
5. **State function:** Any property of the system that defines the state of the system, but is independent of the path that brings about that change in state is known as **state function**. For example, pressure (p), temperature (T), volume (V) and composition or amount (n). The characteristic feature of all state functions is the independence from the method or mechanism by which a change occurs. The variables such as p, T, V, n, etc., are called **state variables**.

   Mathematical criterion for a function to be a state function:

   For any state function $\phi = f(x, y)$ [function of variable x and y] going from initial state A to final state B

   $$\int_A^B \mathrm{d}\phi = \phi_B - \phi_A \qquad \text{[Final state – initial state]}$$

   $$\oint \mathrm{d}\phi = 0 \qquad \text{[as closed integral of any state function is zero]}$$

   or
   $$\frac{\mathrm{d}}{\mathrm{d}y}\left[\frac{\partial\phi}{\partial x}\right]_y = \frac{\mathrm{d}}{\mathrm{d}x}\left[\frac{\partial\phi}{\partial y}\right]_x$$

   or
   $$\mathrm{d}\phi = \left[\frac{\partial\phi}{\partial x}\right]_y \cdot \mathrm{d}x + \left[\frac{\partial\phi}{\partial y}\right]_x \cdot \mathrm{d}y$$

   [where $\left(\frac{\partial\phi}{\partial x}\right)_y$ = partial differential of ϕ w.r.t. x keeping y as constant and so on]

   For example, if pressure is a state function, then,

   $$p = \frac{nRT}{V} = f(T, V)$$

   $$\frac{\partial}{\partial T}\left(\frac{\partial p}{\partial V}\right) = \frac{\partial}{\partial T}\left(\frac{-nRT}{V^2}\right) = \frac{-nR}{V^2}$$

   $$\frac{\partial}{\partial V}\left(\frac{\partial p}{\partial T}\right)_V = \frac{\partial}{\partial V}\left(\frac{nR}{V}\right) = \frac{-nR}{V^2}$$

   $$\frac{\partial}{\partial T}\left(\frac{\partial p}{\partial V}\right)_T = \frac{\partial}{\partial V}\left(\frac{\partial p}{\partial T}\right)_V$$

   Thus, pressure is a state function.
6. **Path functions:** Any property of the system that depends on the initial and final states of the system as well as the path that brings about that change in state is known as path function. For example, work done (w) and heat (q) are path functions. If the path followed is cyclical, then net work done is zero.

> **Note:** In order to define a system, it is not essential to specify all state variables but only a certain number of properties that vary independently from each other. Depending on the nature of the system, once the independent macroscopic properties are fixed, the other dependent state variables get definitive values automatically.

Solved Example 7-1

Show that the volume of a fixed amount of an ideal gas is a state function.

Solution

For an ideal gas $V = \frac{nRT}{T}$, therefore

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{nR}{p} \text{ and } \left(\frac{\partial V}{\partial p}\right)_T = -\frac{nRT}{p^2}$$

We know that $V = f(p, T)$, or

$$\mathrm{d}V = \left(\frac{\partial V}{\partial p}\right)_T \mathrm{d}p + \left(\frac{\partial V}{\partial T}\right)_p \mathrm{d}T$$

we have $$\mathrm{d}V = \frac{-nRT}{p^2}\mathrm{d}p + \left(\frac{nR}{p}\right)_p \mathrm{d}T$$

If V is to be a state function, dV must be an exact differential, for which the Euler's reciprocity condition states that

$$\frac{\partial}{\partial T}\left\{\left(\frac{\partial V}{\partial p}\right)_T\right\}_p = \frac{\partial}{\partial T}\left\{\left(\frac{\partial V}{\partial T}\right)_p\right\}_T$$

$$\frac{\partial}{\partial T}\left\{\left(\frac{\partial V}{\partial p}\right)_T\right\}_p = \frac{\partial}{\partial T}\left(\frac{-nRT}{p^2}\right)_p = \frac{-nR}{p^2}$$

$$\frac{\partial}{\partial T}\left\{\left(\frac{\partial V}{\partial p}\right)_p\right\}_T = \frac{\partial}{\partial T}\left(\frac{nR}{p}\right)_T = \frac{-nR}{p^2}$$

Hence, volume of an ideal gas is a state function.

Types of Thermodynamic Processes

Any process is associated with a change which can be classified as (a) chemical change; (b) phase change and (c) change in p, V, T, etc. A thermodynamic process is said to occur when the state of a system changes from one state (initial state) to another (final state).

1. **Isothermal process:** It is the process carried out at constant temperature, dT = 0. For this process, the system is usually kept in contact with a constant temperature bath (thermostat) and the constant temperature is maintained by the exchange of heat with the thermostat.
2. **Adiabatic process:** It is the process in which heat cannot leave or enter the system, dq = 0. For this process, the system is thermally insulated from the surroundings. However, the temperature of the system may increase or decrease in an adiabatic process.
3. **Isobaric process:** It is the process carried out at constant pressure, dp = 0. All reactions carried out at atmospheric pressure are examples of isobaric process. However, volume change always takes place in an isobaric process.
4. **Isochoric process:** It is the process in which the volume of the system is kept constant (dV = 0). For example, heating of a substance in a non-expanding chamber.
5. **Cyclic process:** It is the process in which the initial and final states are identical. The net work done is not zero in a cyclic process, $w \neq 0$.

All processes can be divided into the following two types:

1. **Reversible process:** It is the process in which the energy change in each step of the process can be reversed in direction by making a small change in any property of the system, such as temperature, pressure, etc. Two important criteria for a process to be reversible are:
   - **(a)** the change must be performed at an infinitesimal slow rate.
   - **(b)** there must be no loss of energy due to friction and no finite temperature differences.

   All reversible processes are hypothetical. System is in equilibrium with surroundings throughout the process. Equation of state can be used throughout the process. For an any reversible process, the change in properties at each step is negligible. For example, consider the cylinder shown in Fig. 7.3 with a massless piston. Here,

   $$p_{\text{ext}} = p_{\text{int}} \pm \mathrm{d}p$$

   where dp is the pressure difference. Then, if dp ° 0, the process is reversible.

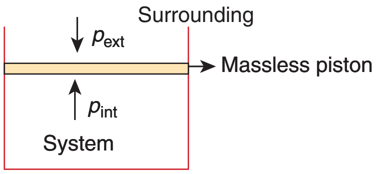


Figure 7.3 Reversible process in a cylinder with massless piston.

2. **Irreversible process:** It is the process in which the system or surroundings are not restored to their initial state at the end of the process. All processes occurring spontaneously in nature are irreversible. They always tend to proceed in a definite direction; and do not proceed in the opposite direction without the action of an external force. Irreversible processes take place spontaneously and not in infinitesimal slow steps that can be reversed. Some examples of irreversible process are expansion and diffusion of gases, flow of heat from a hotter body to a colder body, etc.

In an irreversible process, the system and surrounding are in equilibrium at initial and final state only. So, the equation of state can be used at initial and final state only.

$$p_{\text{ext}} = p_{\text{int}} \pm \Delta p$$

where Δp is appreciable. Here, change in properties at each step is appreciable.

Note: A process is which $p_{\text{ext}} = 0$ or any expansion against vacuum is known as free expansion. It is an irreversible process.

7.2 | THE ZEROTH LAW OF THERMODYNAMICS

Figure 7.4(a) shows two systems labeled A and B. Each is within a container whose adiabatic walls are made from insulation that prevents the flow of heat, and each has the same temperature as indicated by the thermometers. In Fig. 7.4(b), one wall of each container is replaced by a thin silver sheet, and the two sheets are touched together. Silver has a large thermal conductivity, so heat flows through it readily and the silver sheets behave as diathermal walls. Even though the diathermal walls would permit it, no net flow of heat occurs in Fig. 7.4(b), indicating that the two systems are in thermal equilibrium. There is no net flow of heat because the two systems have the same temperature. Two systems are said to be in **thermal equilibrium** if there is no net flow of heat between them when they are brought into thermal contact. We see, then, that *temperature is the indicator of thermal equilibrium in the sense that there is no net flow of heat between two systems in thermal contact that have the same temperature.*

System A is in equilibrium with the thermometer, and so is system B. In each case, the thermometer shows the same temperature. Consequently, systems A and B are found to be in thermal equilibrium with each other and with the thermometer as the third system. The fact that system A and system B are each in thermal equilibrium with this third system at the same temperature means that they are in thermal equilibrium with each other. This establishes the **zeroth law of thermodynamics** which states that

Two systems individually in thermal equilibrium with a third system are in thermal equilibrium with each other.

The zeroth law establishes temperature as the indicator of thermal equilibrium.

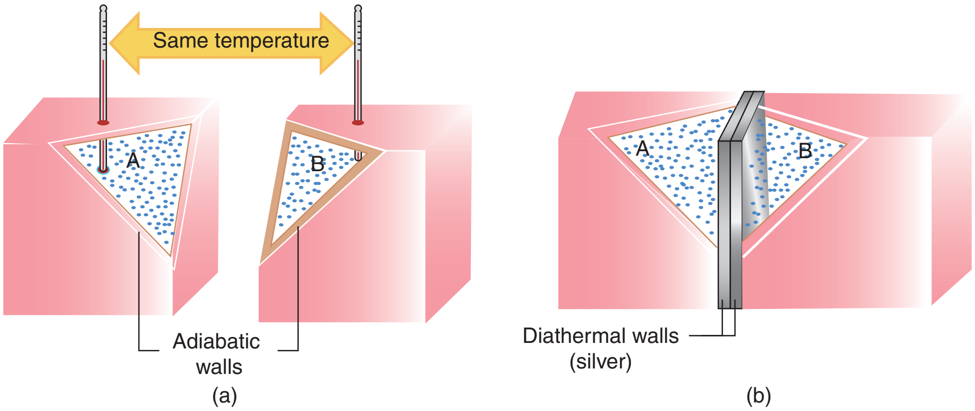


Figure 7.4 (a) Systems A and B are surrounded by adiabatic walls and show the same temperature. (b) When A is put into thermal contact with B through diathermal walls, no net flow of heat occurs between the systems.

7.3 | ENERGY OF THE THERMODYNAMIC SYSTEM

Internal Energy

The total energy contained in a thermodynamic system is called internal energy (U). It includes all forms of kinetic, potential and chemical energies. Kinetic energy is associated with all kinds of motions, such as translational, rotational and vibrational, of the system's particles. Potential energy is associated with static energy of the particles. It also includes chemical energy associated with breaking and making of bonds as well as nuclear energy associated with atomic nuclei and electrical energy associated with charged particles.

Internal energy is due to external factors and due to system itself. Internal energy due to system:

$$U = U_{\text{KE}} + U_{\text{PE}} + U_{\text{Nu}} + U_{\text{M}}$$

where U_{KE} is due to kinetic energy (motion of molecules), U_{PE} is due to potential energy (intermolecular forces), U_{Nu} is due to nuclear energy (binding energy) and U_{M} is due to rest mass energy ($E = m_0C^2$)

Internal energy due to external factors

$$U_{\text{ext}} = U_{\text{g}} + U_{\text{KE}} + \text{some negligible energies}$$

where U_{g} is due to gravitational potential energy and U_{KE} is due to K.E. of center of mass.

Generally, we neglect the external factors as the system is at rest and at the same position. Therefore, total internal energy

$$U = U_{\text{KE}} + U_{\text{PE}} + U_{\text{Nu}} + U_{\text{M}}$$

Now in U_{KE} can be calculated as a function of temperature, that is $U_{\text{KE}} = f(T)$. U_{PE} cannot be calculated without a reference, so $U_{\text{PE}} = f(p, V, T)$. U_{Nu} cannot be calculated and U_{M} can be calculated. Therefore, absolute value of internal energy (U) cannot be calculated. Thus, we calculate ΔU or the change in internal energy as

$$\Delta U = \Delta U_{\text{KE}} + \Delta U_{\text{PE}} + \Delta U_{\text{Nu}} + \Delta U_{\text{M}}$$

Since nucleus and rest mass are constant,

$$\Delta U = \Delta U_{\text{KE}} + \Delta U_{\text{PE}}$$

Mathematical Derivation of ΔU

We know that

$$\Delta U = \underset{\overset{\Rightarrow}{f(T)}}{\Delta U_{\text{KE}}} + \underset{\overset{\Rightarrow}{f(p,V,T)}}{\Delta U_{\text{PE}}}$$

So,

$$\Delta U = f(p, V, T)$$

Now, for any solid, liquid or gas, equation of state exists. Therefore, any two variables out of p, V and T can be expressed in terms of the third variable. Let us consider

$$\Delta U = f(V, T)$$

Since, dU or ΔU is a state function, therefore

$$\mathrm{d}U = \left(\frac{\partial U}{\partial V}\right)_T \mathrm{d}V + \left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T$$

Now,

$$\left(\frac{\partial U}{\partial T}\right)_V = nC_V$$

[The explanation of this expression is covered in the section on heat capacity.]

Therefore,

$$\mathrm{d}U = nC_V\mathrm{d}T + \left(\frac{\partial U}{\partial V}\right)_T \mathrm{d}V$$

Simplified version of the above equation can be obtained for the following cases:

Case 1: For an ideal gas

$$\Delta U = \Delta U_{\text{KE}} + \Delta U_{\text{PE}}$$

Since there is no interaction between molecules of an ideal gas, $\Delta U_{\text{PE}} = 0$. Therefore,

$$\Delta U = f(T)$$

$$\mathrm{d}U = nC_V\mathrm{d}T + \left(\frac{\partial U}{\partial V}\right)_T \int \mathrm{d}V$$

$$\left(\frac{\partial U}{\partial V}\right)_T = 0$$

(Because $U = f(T)$ and if we keep T as constant, the partial differential will be zero as it is simply differentiating a constant.) Therefore,

$$\mathrm{d}U = nC_V\mathrm{d}T$$

The above expression is most commonly used.

Case 2: For any solid or liquid, we know that volume change is negligible for any solid or liquid. Therefore,

$$\mathrm{d}V \cong 0 \text{ and } \mathrm{d}U \cong nC_V\mathrm{d}T$$

Case 3: For a real gas undergoing isochoric process

$$\mathrm{d}V = 0$$
$$\mathrm{d}U = nC_V\mathrm{d}T$$

Case 4: For the real gas undergoing any process except isochoric process

$$\mathrm{d}U = nC_V\mathrm{d}T + \left(\frac{\partial U}{\partial V}\right)_T \cdot \mathrm{d}V$$

We cannot define how much energy is associated with the system in all the above forms of energy, but can only predict and measure the change in internal energy (ΔU). The change in internal energy is given by $\Delta U = U_{\text{final}} - U_{\text{initial}}$ and can occur when work is done either on or by the system, the heat leaves or enters the system or matter enters or leaves the system. The S.I. unit of internal energy is joule (J). It can also be expressed in calories, where 1 cal = 4.184 J.

The internal energy may be a function of temperature of the system and sometimes pressure and volume, chemical nature of the substance. It is a state function, that is, its value depends on the state of the system and not on the path followed to obtain it. For example, the change in internal energy on heating 1 mol of water from 0°C to 100°C is 1.8 kcal. This value depends only on initial and final temperatures, and not on how that temperature is attained.

Work

Work can be defined as the action/displacement of system against some force originating from the surroundings and acting on the boundary of the system. The energy of the system is its capacity to do work and the system may transfer energy to another system or surroundings through work. When work (w) is done by the system, its energy decreases; and when work is done on the system, its energy increases.

Pressure–Volume Work

Consider the gas cylinder with massless piston shown in Fig. 7.5. Here $\vec{F}_{\text{ext}}$ is the external force and $\overrightarrow{\mathrm{d}x}$ is will be the displacement.

Work is defined as the work done by the external force, therefore,

$$w = \vec{F}_{\text{ext}}\overrightarrow{\mathrm{d}x} = F_{\text{ext}} \cdot \mathrm{d}x(\cos 180°)$$
$$= -F_{\text{ext}} \cdot \mathrm{d}x = -p_{\text{ext}} \times A \cdot \mathrm{d}x$$

$$\mathrm{d}w = -p_{\text{ext}}\mathrm{d}V \Rightarrow w = -\int_{V_i}^{V_f} p_{\text{ext}}\,\mathrm{d}V$$

where V_i = initial volume and V_f = final volume.

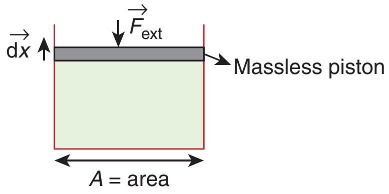


Figure 7.5 Pressure-volume work done by a system.

Units of work:

$$1 \text{ atm liter} = 1.01325 \times 10^5 \text{ Pa} \times 10^{-3} \text{ m}^3$$
$$= 1.01325 \times 10^2 \text{ J} = 101.325 \text{ J}$$
$$1 \text{ bar liter} = 10^5 \text{ Pa} \times 10^{-3} \text{ m}^3 = 100 \text{ J}$$

Sign convention:

Work done on the system = +ve
Work done by the system = –ve

Work done during expansion

For expansion, dV is positive, therefore, work done is negative.

$$w = -\int \underset{+\text{ve}}{\underset{\downarrow}{p_{\text{ext}}}}\, \underset{+\text{ve}}{\underset{\downarrow}{\text{d}V}} = -\text{ve}$$

Work done during compression

For compression, dV is negative, therefore, work done is positive.

$$w = -\int \underset{+\text{ve}}{\underset{\downarrow}{p_{\text{ext}}}}\, \underset{-\text{ve}}{\underset{\downarrow}{\text{d}V}} = +\text{ve}$$

We will consider the mechanical or pressure–volume work done by a system. Consider an ideal gas (1 mol) taken in an insulated cylinder fitted with a frictionless piston. The system (the gas) starts from an *initial state i*, described by a pressure p_i, a volume V_i and a temperature T_i and we want to change the system to a *final state f*, described by a pressure p_f, a volume V_f and a temperature T_f.

The procedure by which we change the system from its initial state to its final state is called a **thermodynamic process**. In such a process, energy may be transferred into the system from a thermal reservoir (positive heat) or vice versa (negative heat). Also, work can be done by the system to raise the loaded piston (negative work) or lower it (positive work). We assume that all such changes occur slowly, with the result that the system is always in (approximate) thermal equilibrium (i.e., every part of the system is always in thermal equilibrium with every other part).

Suppose also that we allow the gas to expand from an initial volume V_i to a final volume V_f, while we keep the temperature T of the gas constant. Such a process, at *constant temperature,* is called an **isothermal expansion** (and the reverse is called an **isothermal compression**).

If the external pressure p_ext on the system is slightly less than the internal pressure of the gas p, then the piston would move outwards till both the pressures become equal. Let this isothermal expansion take place in a single step so that the final state of the system is reached. If the piston has moved through distance l and the cross-sectional area of the piston is A, then change in volume of gas is

$$\Delta V = (V_f - V_\text{i}) = l \times A$$

The force on the piston can be obtained as

$$\text{Pressure} = \frac{\text{Force}}{\text{Area}} \Rightarrow \text{Force} = \text{Pressure} \times \text{Area} = p_\text{ext} \times A$$

The work done by the piston is

$$w = \text{Force} \times \text{Distance} = -p_\text{ext} \times A \times l = -p_\text{ext} \times \Delta V$$

The negative sign of work indicates that in isothermal expansion work is done by the system (Fig. 7.6).

If the external pressure on the gas is greater than the internal pressure of the gas, the piston move inwards and isothermal compression takes place. The work done is given by

$$w = \text{Force} \times \text{Distance} = -p_\text{ext} \times A \times l = -p_\text{ext} \times (-\Delta V)$$

The negative sign is used because the volume decreases if the system is compressed. This will also yield the required conventional sign for work because work done on the system is positive. We can thus conclude that in compression, work is done on the system.

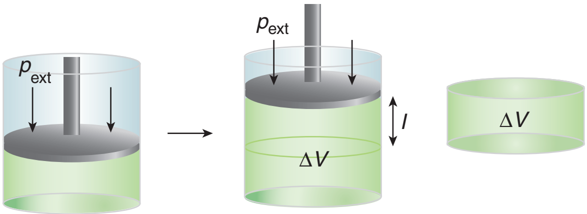


Figure 7.6 Work done by an ideal gas when the system undergoes isothermal expansion under constant external pressure p_ext.

During the change in volume, the pressure of the gas may also change. In that case, the volume does not change to V_f in a single step but through finite number of steps, each of which involves small change in pressure (Fig. 7.7). The work done is measured corresponding to each change and summed up to give the total work done by the gas as

$$w = \sum p_{\text{ext}} \times \Delta V$$

If the process take place in a manner that pressure at each stage decreases by an infinitesimal amount dp and the volume increases by an infinitesimal amount dV, then the total work done by the gas can be obtained by the relation

$$w = -\int_{V_i}^{V_f} p_{\text{ext}}\, \mathrm{d}V \tag{7.1}$$

The external pressure at each stage is equal to $p - \mathrm{d}p$ (or $p + \mathrm{d}p$ in case of compression). By definition, such processes where the properties at each step undergo infinitesimal change are called **reversible processes**.

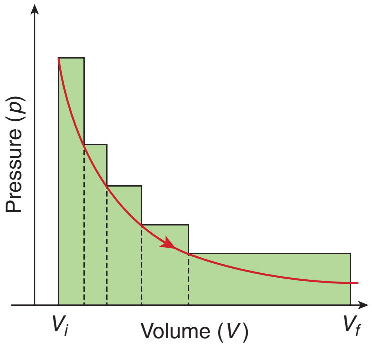


Figure 7.7 Pressure–volume plot when pressure changes in finite steps during expansion from initial volume (V_i) to final volume (V_f).

To evaluate the integral in Eq. (7.1) directly, we would need to know how pressure varies with volume for the actual process by which the system changes from state i to state f. We can plot the pressure of the gas versus its volume to obtain a pV diagram as shown in Fig. 7.8a.

In Fig. 7.8(a), the curve indicates that the pressure decreases as the volume increases. The integral in Eq. (7.1) (and thus, the work w done by the gas) is represented by the shaded area under the curve between points i and f. Regardless of what exactly we do to take the gas along the curve, that work is negative, due to the fact that the gas increases its volume by forcing the piston upwards.

Figure 7.8(b) shows an example in which positive work is done by a system as some external force compresses the system, reducing its volume. The absolute value of the work done is still equal to the area beneath the curve, but because the gas is *compressed,* the work done by the gas is negative.

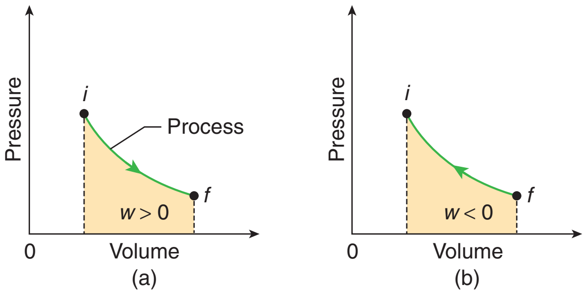


Figure 7.8 (a) pV diagram for a system from state i to state f. (b) pV diagram for a system from state f to state i. Shaded region representing work done.

In chemistry, it is important to relate the work term to the internal pressure of the system rather than the external pressure applied. So for a reversible chemical system, Eq. (7.1) can be written as

$$w_{\text{rev}} = -\int_{V_i}^{V_f} p_{\text{ext}}\, \mathrm{d}V = -\int_{V_i}^{V_f} (p \pm \mathrm{d}p)\, \mathrm{d}V$$

Since value of $\mathrm{d}p \times \mathrm{d}V$ is small, we can write

$$w_{\text{rev}} = -\int_{V_i}^{V_f} p\,\mathrm{d}V \tag{7.2}$$

Using the ideal gas equation, we can express pressure in terms of volume for n moles of gas as

$$pV = nRT$$

or

$$p = \frac{nRT}{V}$$

Substituting for p in Eq. (7.2), we get

$$w_{\text{rev}} = -\int_{V_i}^{V_f} \frac{nRT}{V}\mathrm{d}V = -nRT \ln\frac{V_f}{V_i} \tag{7.3}$$

because for an isothermal process, temperature is constant. The work done by the gas can be expressed as

$$w_{\text{rev}} = -2.303\ nRT\ \log\frac{V_f}{V_i} \tag{7.4}$$

For an expansion, V_f is greater than V_i, so the ratio V_f/V_i in Eq. (7.4) is greater than unity. The natural logarithm of a quantity greater than unity is positive, and so the work done, w, by an ideal gas during an isothermal expansion is negative, as we expect. For a compression, V_f is less than V_i, so the ratio of volumes in Eq. (7.4) is less than unity. The natural logarithm in that equation – hence the work w – is positive, again as we expect.

Note: Equation (7.4) does not give the work done, w, by an ideal gas during *every* thermodynamic process. Instead, it gives the work only for a process in which the temperature is held constant. If the temperature varies, then the symbol T in Eq. (7.3) cannot be moved in front of the integral symbol as in Eq. (7.4).

Adiabatic Work

Consider an insulated beaker containing water or hot water in an insulated flask thermos flask. This adiabatic system will undergo a change of state without exchange of heat between system and surroundings, and such a process is known as an **adiabatic process**. The wall (in this case the beaker) separating the adiabatic system from the surroundings is known as an **adiabatic wall**. Let this state of the system be defined as state A with temperature T_A and internal energy U_A. The state of the system can be changed to new state without loss or gain of heat, by doing mechanical or electrical work. Some experiments were conducted by J.P. Joule in 1840s, which led him to conclude that the same amount of work done on the system produces the same change in state (measured as temperature in this case), irrespective of how the change is brought about. We can thus define internal energy as a state function, where change from one state (U_1) to another (U_2) can be brought about by doing adiabatic work on the system. Therefore,

$$\Delta U = U_2 - U_1 = w_{\text{adiabatic}}$$

The work term $w_{\text{adiabatic}}$ is positive when work is done on the system and negative when work is done by the system.

Work may also be in the form of expansion or compression of system known as the pressure–volume work. The volume change in expansion of solids and liquids is small, so the work done is small. However, in case of gases, the volume change is substantial and work done by gas in the system is equal to the change in volume against pressure p.

$$w = -p\Delta V$$

Consider the example of a gas taken in a cylinder fitted with a movable piston. In the equilibrium state, the pressure applied on the gas is equal to the pressure of the gas. If the pressure of the gas is lowered, the gas inside the cylinder expands and pushes the piston till the pressure of the gas becomes equal to the pressure on the gas. The work in this case is done by the system at the expense of the internal energy. In another situation, if the external pressure on the gas is increased, the volume of the gas inside the cylinder will decrease. The piston is pushed down as a result and work is done on the system, which increases the internal energy of the system.

Heat

The internal energy of the system can also be changed by supplying heat to the system or removing heat from it without doing any work on the system or by the system. The energy transferred because of temperature difference between two systems is called heat. It flows from system at higher temperature to the one at lower temperature. The amount of heat transferred (q) is proportional to the difference in temperatures.

Generally heat transfer involves temperature change (except phase change/chemical change). We define molar heat capacity (C) as the heat required to raise the temperature of a substance by 1K for 1 mole of the substance.

$$C = \frac{q}{n\mathrm{d}T}$$

$$q = nC\mathrm{d}T = ms\mathrm{d}T$$

C is a path function, that is, process dependent.

Some important expressions related to molar heat capacity are listed as follows:

1. We define C_p as the molar heat capacity for an isobaric process as

$$C_p = \frac{q_p}{n\mathrm{d}T} = \frac{1}{n}\left(\frac{\partial H}{\partial T}\right)_p$$

(Here we use $q_p = \mathrm{d}H$; this will be covered in the section on Enthalpy.)

2. We define, C_V as molar heat capacity for an isochoric process as

$$C_V = \frac{q_V}{n\mathrm{d}T} = \frac{1}{n}\left(\frac{\partial U}{\partial T}\right)_V$$

(Here we use $q_V = \mathrm{d}U$.)

3. Molar heat capacity is a function of T for an ideal gas

$$C = a + bT + CT^2 + dT^3 + \ldots$$

Here, a, b, c and d are constants whose values decrease as T increases.

4. For solids and liquids C_p and C_V are same for any ideal gas

$$C_p - C_V = R$$

5. Relation of degree of freedom with C_p and C_V

   (a) The translational degree of freedom $f_{\text{trans}} = 3$ (always). Contribution by 1 f_{trans} towards $C_V = R/2$.

   (b) For the rotational degree of freedom, f_{rot}, the value will vary with the atomicity. Contribution by 1 f_{rot} towards $C_V = R/2$

   (c) Vibrational degree of freedom, f_{vib} is to be taken into account only at higher temperature. It is calculated as $f_{\text{vib}} = f_{\text{total}} - f_{\text{trans}} - f_{\text{rot}}$. Contribution of 1 f_{vib} towards $C_V = R$

   (d) Total degrees of freedom $f_{\text{total}} = 3N$, where N = no. of atoms or atomicity.

   (e) Poisson's ratio $\gamma = \dfrac{C_p}{C_V}$

   (f) The values for degree of freedom and C_V for molecules with different atomicity are summarized below in Table 7.1

Table 7.1 Relation between atomicity and degree of freedom

Atomicity	f_{trans}	f_{rot}	f_{vib}	f_{total}	C_V	
					At high T	At low T
Monoatomic	3	0	0	3	$3R/2$	$3R/2$
Diatomic	3	2	1	6	$7R/2$	$5R/2$
Triatomic (linear)	3	2	4	9	$13R/2$	$5R/2$
Triatomic (non-linear)	3	3	3	9	$6R$	$3R$

In all the above cases

$$C_p = C_V + R \text{ and } \gamma = \frac{C_p}{C_V}$$

Note: For a mixture

$$C_{p_{\text{mix}}} = \frac{\Sigma n_i (C_{p_i})}{\Sigma n_i} \text{ and } C_{V_{\text{mix}}} = \frac{\Sigma n_i (C_{V_i})}{\Sigma n_i}$$

where n_i is the number of moles.

$$\gamma_{\text{mix}} = \frac{\Sigma n_i (C_{p_i})}{\Sigma n_i (C_{V_i})} \neq \frac{\Sigma n_i \gamma_i}{\Sigma n_i}$$

Consider a system which can exchange heat with the surroundings through thermally conducting walls, instead of adiabatic walls. We can take water at temperature T_1 in a container with thermally conducting walls, say a copper container, and place it in a reservoir of temperature at temperature T_2. Heat absorbed by the system can be measured in terms of the temperature difference between the container and the reservoir, that is, $T_2 - T_1$. The change in internal energy is equal to the heat exchanged when no work is done by the system. Therefore,

$$\Delta U = q$$

The quantity of heat is expressed in calories. Here, 1 cal is defined as the amount of heat required to raise the temperature of 1 g of water by 1°C at 15°C.

Note: Work and heat conventions:

q is (+)	Heat is absorbed by the system.	q is (−)	Heat is released by the system.
w is (+)	Work is done on the system.	w is (−)	Work is done by the system.

Solved Example 7-2

One mole of an ideal gas is put through a series of changes as shown in the graph in which A, B, C mark the three stages of the system. At each stage, the variables are shown in Fig. 7.9.

(a) Calculate the pressure at three stages of the system.

(b) Name the processes during the following changes: (i) A to B, (ii) B to C, (iii) C to A, and (iv) overall change.

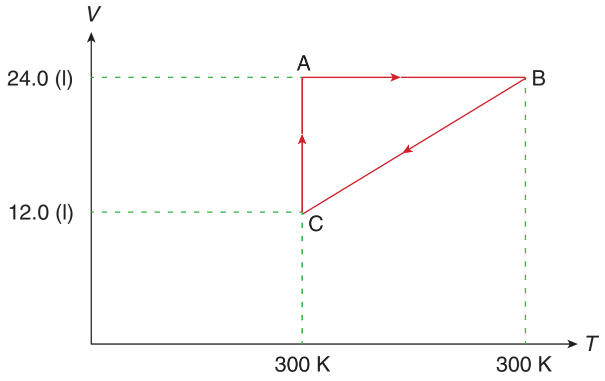


Figure 7.9

Solution

(a) **At stage A:** Given that $V = 24$ L; $T = 300$ K; $n = 1$ mol; $R = 0.0821$ L atm K^{-1} mol^{-1}. Substituting these values in the ideal gas equation,

$$p = \frac{1 \times 0.0821 \times 300}{24} = 1.026\,\text{atm}$$

At stage B: Volume remains the same but temperature change from 300 K to 600 K. Thus, according to pressure law, the pressure will be double at B with respect to A.

Pressure at B = 2 × 1.026 = 2.052 atm

At stage C: Temperature is 300 K and volume is half that of stage A. Thus, according to Boyle's law, the pressure at C will be double with respect to A.

Pressure at C = 2 × 1.026 = 2.052 atm

(b) **(i)** During the change from A to B, volume remains constant, the process is isochoric.

(ii) During the change from B to C the pressure remains constant, the process is isobaric.

(iii) During the change from C to A, the temperature remains constant, the process is isothermal.

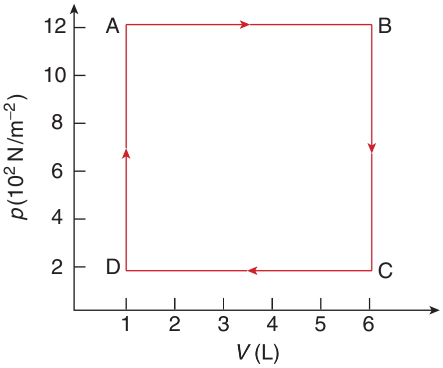
(iv) Overall, the process is cyclic as it returns to its initial state.

Solved Example 7-3

The diagram shows a p–V graph of a thermodynamic behavior of an ideal gas. Find out from the following graph:

(a) Work done in the process A → B, B → C, C → D and D → A.

(b) Work done in the complete cycle A → B → C → D → A.



Solution

Work done in the process A → B (the process is expansion, net work is done by the gas)

$$w_{A\to B} = -p\times\Delta V = -12\times 10^5\times 5\times 10^{-3} = -6000\,\text{J}$$

Work done in the process B → C, $w_{B\to C} = 0$ as volume remains constant.
Work done in the process C → D (the process is contraction, hence work is one on the gas)

$$w_{C\to D} = p\times\Delta V = 2\times 10^5\times 5\times 10^{-3} = 1000\ \text{J}$$

Work done in the process D → A, $w_{D\to A} = 0$ as volume remains constant.
Net work done in the whole cycle = –6000 + 1000 = –5000 J
This is the net work done by the gas.

7.4 | THE FIRST LAW OF THERMODYNAMICS

The first law of thermodynamics is an application of the law of conservation of energy, which states that energy can neither be created nor destroyed, that is, the total energy of the system remains constant, though it may change from one form to another. Another statement for the first law arises from the fact that it is impossible to construct a perpetual motion machine that can produce work without spending energy.

Mathematical Derivation of First Law

Let us consider the case where the change in state of the system is brought about both by doing work and transfer of heat. Then the change in internal energy is given by

$$\Delta U = q + w \tag{7.5}$$

For this change in state, q and w will depend on how the change takes place. So these are not state functions. However, the change in internal energy ΔU does not depend on how a change takes place and will depend only on the initial and final states of the system. If there is no transfer of heat to or from the system ($q = 0$) or no work is done on or by the system ($w = 0$), then $\Delta U = 0$.

The first law of thermodynamics is an application of the law of conservation of energy, which states that energy can neither be created nor destroyed, that is, the total energy of the system remains constant, though it may change from one form to another.

Suppose heat q is supplied to the system with initial internal energy U_1. A part of heat energy is used by the system to do work ($-w$) while the remaining is used to change the internal energy of the system to U_2. According to first law of thermodynamics,

$$\Delta U = U_2 - U_1 = q + w$$
$$q = \Delta U - (-w)$$

So the energy of the system is conserved. For an infinitesimally small change dU in energy, the corresponding changes in heat and work are given by dq and dw and Eq. (7.6) can be written as:

$$\mathrm{d}U = \mathrm{d}q + \mathrm{d}w \tag{7.6}$$

Equations (7.5) and (7.6) are mathematical expressions for the first law of thermodynamics.

Solved Example 7-4

A system moves from state A to state B by a certain path, such that q and w are found to be +670 cal and –209.3 cal, respectively. Calculate ΔU of the system.

Solution

The first law of thermodynamics can be mathematically expressed as

$$\Delta U = q + w$$

Therefore, the change in internal energy can be calculated as

$$\Delta U = q + w = 670 - 290.3 = +460.7 \text{ cal}$$

Solved Example 7-5

A certain system absorbs 0.300 kJ of heat and has 0.700 kJ of work performed on it. What is the value of ΔU for the change? Is the overall change exothermic or endothermic

Solution

$$\Delta U = q + w = 0.300 \text{ kJ} + 0.700 \text{ kJ} = +1.000 \text{ kJ}$$

The overall process is endothermic, meaning that the internal energy of the system increases. Notice that both terms, q and w, contribute to the increase in internal energy of the system; the system gains heat ($+q$) and has work done on it ($+w$).

Solved Example 7-6

Using first law of thermodynamics, show that heat is not a state function.

Solution

The essential criteria of a state function is that it must be a perfect differential. From the first law of thermodynamics, if the work is done by the system, then

$$\mathrm{d}U = \mathrm{d}q - \mathrm{d}w \tag{1}$$

Also, work can be expressed in terms of pressure–volume work as

$$\mathrm{d}w = p\mathrm{d}V$$

Therefore,

$$\mathrm{d}q = \mathrm{d}U + p\mathrm{d}V \tag{2}$$

Taking E as a function of T and V, differential can be written as:

$$\mathrm{d}U = \left(\frac{\partial U}{\partial V}\right)_T \mathrm{d}V + \left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T$$

Using this in Eq. (2), we get

$$\mathrm{d}q = \left(\frac{\partial U}{\partial V}\right)_T \mathrm{d}V + \left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T + p\mathrm{d}V \tag{3}$$

At constant T, divide Eq. (3) by dV:

$$\left(\frac{\partial q}{\partial V}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T + p \tag{4}$$

Similarly at constant V, divide Eq. (3) by dT:

$$\left(\frac{\partial q}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V \tag{5}$$

Now, if heat (q) is a state function, then the following must be true from Euler's reciprocal relation:

$$\left(\frac{\partial^2 q}{\partial T \partial V}\right) = \left(\frac{\partial^2 q}{\partial V \partial T}\right) \tag{6}$$

Evaluating the second differentials of Eqs. (5) and (6), we get

$$\left(\frac{\partial^2 U}{\partial T \partial V}\right) + \left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial^2 U}{\partial V \partial T}\right) \tag{7}$$

Since E is a state function, from Euler's relation we have

$$\left(\frac{\partial^2 U}{\partial T \partial V}\right) = \left(\frac{\partial^2 U}{\partial V \partial T}\right) \tag{8}$$

Using Eqs. (8) in Eq. (7), we get

$$\left(\frac{\partial p}{\partial T}\right)_V = 0$$

This means that pressure is independent of temperature at constant volume. But this is contrary to Charles law, which states that at constant volume, the pressure of gas is directly proportional to its Kelvin temperature

$$\left(\frac{\partial p}{\partial T}\right)_V = K \neq 0$$

Hence, the assumption that q is a state function, is proven wrong; so q is not a state function.

Solved Example 7-7

The value of ΔU for a certain change is –1455 J. During the change, the system absorbs 812 J of heat. Did the system do work, or was work done on the system? How much work, expressed in joules, was involved?

Solution

From the first law of thermodynamics, we have $\Delta U = q + w$. So,

$$-1455 = 812 + w \Rightarrow w = -2267 \text{ J}$$

Since w is defined to be the work done on the system by the surroundings, then in this case, a negative amount of work is done on the system by the surroundings. This implies that the system, in fact, does work on the surroundings.

7.5 | CALCULATION OF WORK DONE IN DIFFERENT PROCESSES

Work done by a system under different thermodynamic processes is discussed and derived as follows.

1. Work done by an ideal gas in an irreversible expansion against a constant external pressure p_{ext} (isobaric expansion).

   Let the initial volume of gas be V_i and the final volume of gas be V_f. Then

$$w = -\int_{V_i}^{V_f} p_{\text{ext}}\, dV = -p_{\text{ext}} \int_{V_i}^{V_f} dV$$

   as p_{ext} is constant. Then

$$w = -p_{\text{ext}}(V_f - V_i) = -p_{\text{ext}}\Delta V$$

   The work done is given by the area under the pressure-volume curve (Fig. 7.10). The negative sign indicates that the gas is expanding.

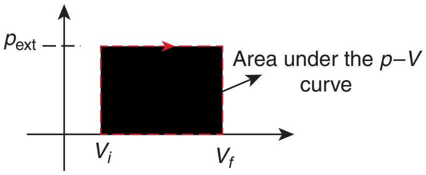


Figure 7.10 Pressure-volume curve for irreversible expansion under constant pressure.

2. Work done by an ideal gas in a reversible isobaric process during expansion.

   Let the initial volume of gas be V_i and the final volume of gas be V_f. Then

$$w = -\int p_{\text{ext}}\, dV = \int p dV$$

   Because for a reversible process, $p_{\text{ext}} = p_{\text{gas}} = p$ (say).

$$w = -p\int_{V_i}^{V_f} dV \qquad \text{(as } p \text{ is constant for an isobaric process)}$$

$$w = -p(V_f - V_i) = -p(\Delta V)$$

   The work done is given by the area under the pressure-volume curve (Fig. 7.11). The negative sign indicates that the gas is expanding.

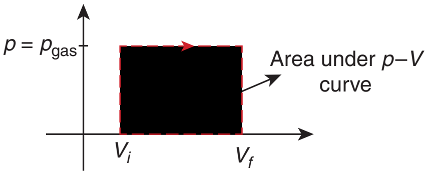


Figure 7.11 Pressure-volume curve for reversible expansion under constant pressure.

Note: During expansion $p_{\text{gas}} \geq p_{\text{ext}}$.

Figure 7.12 shows the pressure-volume curve for work done during reversible and irreversible expansion process. Area under curve during reversible process is greater than the area under curve during irreversible process. Also, in both the cases, the work done is negative. Therefore, work done by the gas in reversible process is always greater in irreversible process. Thus, reversible processes are more efficient.

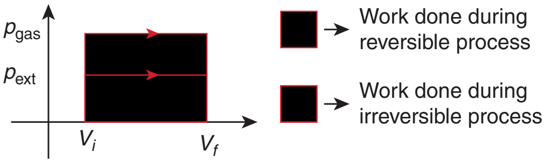

p_{gas}
p_{ext}
V_i
V_f
Work done during reversible process
Work done during irreversible process

Figure 7.12 Work done during reversible and irreversible expansion process.

3. Work done by an ideal gas in reversible/irreversible isochoric process.

   For an isochoric process dV = 0. Therefore, work done

$$w = -\int p_{\text{ext}}\, \mathrm{d}V = 0$$

4. Work done by an ideal gas in reversible isothermal expansion at temperature T.

   Given that, initial volume = V_i, final volume = V_f and number of moles of gas = n. Then work done

$$w = -\int p_{\text{ext}}\, \mathrm{d}V$$

$$w = -\int p\, \mathrm{d}V$$

   Because for reversible process $p_{\text{ext}} = p_{\text{gas}} = p$ (say). Therefore,

$$w = -\int_{V_i}^{V_f} \frac{nRT}{V}\mathrm{d}V$$

   Because for an ideal gas, $p = \dfrac{nRT}{V}$, we have

$$w = -nRT\int_{V_i}^{V_f}\left(\frac{1}{V}\right)\mathrm{d}V$$

   As for an isothermal process, T is constant.

$$w = -nRT\ln\left(\frac{V_f}{V_i}\right)$$

5. Work done by an ideal gas in reversible adiabatic expansion.

   Given that, initial pressure = p_i, final pressure = p_f, initial volume = V_i, final volume = V_f, Poisson's ratio = γ, initial temperature = T_i, final temperature = T_f and number of moles of gas = n. Also, C_V is given. Since the process is adiabatic, pV^{γ} = constant = k, therefore,

$$p_iV_i^{\gamma} = k \text{ or } p_i = kV_i^{-\gamma} \tag{7.7}$$

$$p_fV_f^{\gamma} = k \text{ or } p_f = kV_f^{-\gamma} \tag{7.8}$$

   So work done is

$$w = -\int p_{\text{ext}}\, \mathrm{d}V$$

$$w = -\int p\mathrm{d}V$$

Because for a reversible process, $p_{\text{gas}} = p_{\text{ext}} = p$ (say).

$$w = -\int_{V_i}^{V_f} kV^{-\gamma}\,\mathrm{d}V$$

For a reversible process, $pV^{\gamma} = k$, therefore,

$$\begin{aligned}
w &= \left.\frac{-kV^{-\gamma+1}}{-\gamma+1}\right|_{V_i}^{V_f} \\
&= \frac{kV_f^{-\gamma+1} - kV_i^{-\gamma+1}}{\gamma-1} \\
&= \frac{(kV_f^{-\gamma})(V_f) - (kV_i^{-\gamma})(V_i)}{\gamma-1} \\
&= \frac{p_fV_f - p_iV_i}{\gamma-1} \qquad \text{(from Eqs. 7.7 and 7.8)} \\
&= \frac{nR(T_f - T_i)}{\gamma-1} = n\left(\frac{R}{\gamma-1}\right)(\Delta T) = nC_V\Delta T \qquad \text{(as gas is ideal)}
\end{aligned}$$

As, $\dfrac{C_p}{C_V} = \gamma$ and $C_p - C_V = R$. Therefore,

$$C_V = \frac{R}{\gamma-1}$$

The above expression can also be calculated simply by using first law of thermodynamics.

6. Work done in free expansion.

   Here, $p_{\text{ext}} = 0$, therefore,

$$w = -\int p_{\text{ext}}\,\mathrm{d}V = 0$$

7. Work done in any reversible polytropic process by an ideal gas.

   pV^x = constant

   For $x = 1$, pV = constant, implies process is isothermal.

   $x = y$, PV^y = constant, implies process is adiabatic.

   $x = \infty$, V = constant, implies process is isochoric.

   $x = 0$, p = constant, implies process is isobaric.

   The work done is given by

$$w = \frac{p_2V_2 - p_1V_1}{x-1} = \frac{nR\Delta T}{x-1}$$

The gas is ideal, so $\Delta U = nC_V\,\Delta T$

Also, from first law of thermodynamics $\Delta U = q + w$. Therefore,

$$nC_V\Delta T = q + \frac{nR\Delta T}{x-1}$$

Also $q = nC\Delta T$, therefore,

$$nC_V\Delta T = nC\Delta T + \frac{nR\Delta T}{x-1}$$

$$C = C_V + \frac{R}{1-x}$$

Note: For any general process $dU = q + w$. Therefore, for one mole of gas

$$C_V dT = C dT - p_{\text{ext}} dV$$

$$C = C_V + p_{\text{ext}}\left(\frac{dV}{dT}\right)$$

8. Work done in a cyclic process

All cyclic processes are reversible, so the work done is area under the pressure-volume curve for a cyclic process (Fig. 7.13).

$$\text{Work done} = -(p_2 - p_1)\,(V_2 - V_1)$$

To assign the sign convention for work in a cyclic process,

$w_{1-2} = 0$
$w_{2-3} =$ negative work
$w_{3-4} = 0$
$w_{4-1} =$ positive work

Therefore, net area under the curve is negative. For any cyclic process, the total work done is negative if the cyclic process is clockwise and is positive if the cyclic process in anticlockwise.

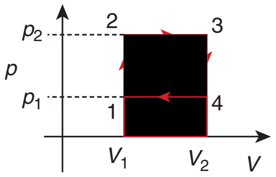


Figure 7.13 Pressure-volume curve for a cyclic process.

Solved Example 7-8

A gas expands against a variable external pressure given by $p = 10/V$ atm, where V is the volume at each stage of expansion. In expanding from 10 L to 100 L, the gas undergoes a change in internal energy $\Delta U = 418$ J. How much heat has been absorbed?

Solution

For an isothermal process, work done in an expansion is given by

$$w = -\int_{V_1}^{V_2} p\,dV$$

Given that $p = 10/V$; $V_1 = 10$ L and $V_2 = 100$ L. Substituting in the equation, we get

$$w = -\int_{V_1}^{V_2} \frac{10}{V}\,dV = -\int_{V_1}^{V_2} 10\frac{dV}{V} = -10\ln\frac{V_2}{V_1}$$

$$= -10\ln\frac{100}{10} = -10 \times 2.303\log 10 = 23.03\,\text{L atm} = -2332.9\text{ J}$$

According to the first law of thermodynamics, $\Delta U = q + w$

or $$q = \Delta U - w$$

Given that $\Delta U = 418$ J and $w = -2332.9$ J, therefore

$$q = 418 - (-2332.9\text{ J}) = 2.76\text{ kJ}$$

Solved Example 7-9

Consider the reaction between aqueous solutions of baking soda, $NaHCO_3$, and vinegar, CH_3COOH.

$$NaHCO_3(aq) + CH_3COOH(aq) \rightarrow$$
$$CH_3COONa(aq) + H_2O(l) + CO_2(g)$$

If this reaction occurs at atmospheric pressure ($p = 1$ atm), how much work, expressed in L atm, is done by the system in pushing back the atmosphere when 1.00 mol $NaHCO_3$ reacts at a temperature of 25°C?

Solution

This is a reaction that produces 1 mol of a single gaseous product, CO_2. Furthermore, this mole of gaseous product forms from non-gaseous materials. The volume that will be occupied by this gas, once it is formed, can be found by application of Charles' law:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

or $$V_2 = 22.4\text{ L} \times \frac{298\text{ K}}{273\text{ K}} = 24.5\text{ L}$$

The work done by the system in pushing back the atmosphere on forming the products is

$$w = -p\Delta V = -(1.00\text{ atm})(24.5\text{ L}) = -24.5\,\text{L atm}$$

Solved Example 7-10

If 22 g of CO_2, showing ideal behavior, expand isothermally and reversibly from 2.5 L to 7.5 L at 27°C, then calculate the work done and heat absorbed.

Solution

For an ideal gas, work done in isothermal and reversible expansions is given by

$$w = -nRT \ln\frac{V_2}{V_1} = -2.303\,nRT \log\frac{V_2}{V_1}$$

Given that $V_1 = 2.5\,\text{L}; V_2 = 7.5\,\text{L}; T = 27°\text{C} = 273 + 27 = 300\,\text{K}$; $R = 8.314\,\text{J K}^{-1}\text{mol}^{-1}$ and $n = 22/44 = 0.5$ mol. Substituting these values in the equation, we get

$$w = 2.303 \times 0.5 \times 8.314 \times 300 \times \log\frac{7.5}{2.5} = -1370.3\ \text{J}$$

According to first law of thermodynamics, $\Delta U = q + w$ Since $\Delta U = 0$ for an ideal gas undergoing reversible isothermal expansion, $q = -w = +1370.3$ J.

7.6 | ENTHALPY OR HEAT CONTENT, *H*

Most of the chemical reactions in gaseous state proceed under constant atmospheric pressure, so thermodynamic changes need to be evaluated at constant pressure conditions. Consider a change in the system from initial state (1) to the final state (2), carried out at constant pressure. The amount of heat absorbed during the process is q and the volume increases from V_1 to V_2. Then, according to first law of thermodynamics, we have

$$\Delta U = q + w = q_p - p\Delta V$$

Here, q_p represents the heat absorbed by the system at constant pressure and $p\Delta V$ represents the expansion work done by the system. The equation can be rewritten as

$$U_2 - U_1 = q_p - p(V_2 - V_1)$$

On rearranging, we get

$$q_p = (U_2 - U_1) + p(V_2 - V_1) \tag{7.9}$$

Equation (7.9) can be rewritten as

$$q_p = (U_2 + pV_2) - (U_1 + pV_1) = H_2 - H_1 = \Delta H$$

The quantity $U + pV$ is known as heat content or enthalpy (H) of the system and ΔH is the enthalpy change for the process. Since U, p and V are state functions, H must also be a state function, that is, it does not depend on the path followed to reach the final state.

Mathematical Derivation of Δ*H*

Enthalpy (H) is defined as change which relates to heat capacity constant pressure. It is given by

$$H = U + pV$$
$$\mathrm{d}H = \underset{f(p,V,T)}{\underset{\downarrow}{\mathrm{d}U}} + \underset{f(p,V)}{\underset{\downarrow}{\mathrm{d}(pV)}}$$

Therefore,

$$\mathrm{d}H = f(p, V, T)$$

Since equation of state exists, so dH can be expressed as $f(p, V)$ or $f(V, T)$ or $f(p, T)$
Thus, d$H = f(p, T)$. As H is a state function, so

$$\mathrm{d}H = \left(\frac{\partial H}{\partial T}\right)_p \cdot \mathrm{d}T + \left(\frac{\partial H}{\partial p}\right)_T \cdot \mathrm{d}p$$

Now,

$$\left(\frac{\partial q_p}{\partial_T}\right)_p = \left(\frac{\partial H}{\partial T}\right)_p = nC_p$$

Therefore,

$$\mathrm{d}H = nC_p\mathrm{d}T + \left(\frac{\partial H}{\partial p}\right)_T \cdot \mathrm{d}p \qquad (7.10)$$

Equation (7.10) can be simplified for the following cases:

1. For an ideal gas.

$$H = U + pV$$

$$\underset{\substack{\Rightarrow \\ f(T)}}{H} = \underset{\substack{\Rightarrow \\ f(T)}}{U} + \underset{\substack{\Rightarrow \\ f(T)}}{nRT}$$

Therefore,

$$\left(\frac{\partial H}{\partial p}\right)_T = 0 \qquad [\text{as } H = f(T)]$$

$$\mathrm{d}H = nC_p\mathrm{d}T$$

This is the most commonly used expression for calculation of ΔH.

2. For a real gas undergoing isobaric process.

Here, $\mathrm{d}p = 0$. Therefore,

$$\mathrm{d}H = nC_p\mathrm{d}T$$

3. For solids and liquids.

Here

$$\left(\frac{\partial H}{\partial p}\right)_T \cong 0$$

Because there is only external pressure acting on solid and liquid and it does not affect properties of solid. Therefore,

$$\mathrm{d}H \cong nC_p\mathrm{d}T$$

Change in enthalpy of a system from state 1 to state 2 can be expressed as

$$\Delta H = H_2 - H_1$$

Substituting values for initial and final states, we get

$$\Delta H = (U_2 + p_2V_2) - (U_1 + p_1V_1) = (U_2 - U_1) + (p_2V_2 - p_1V_1)$$

or

$$\Delta H = \Delta U + \Delta pV$$

At constant pressure conditions

$$\Delta H = \Delta U + p\Delta V \qquad (7.11)$$

or

$$\Delta H = \Delta U + w$$

Comparison of Eq. (7.11) with the expression for first law [Eq. (7.1)] shows that enthalpy can be equated with energy supplied as heat (or absorbed) at constant pressure, that is $\Delta H = q_p$.

At constant volume, no pressure–volume work is done, so $p\Delta V = 0$ and the expression for enthalpy becomes

$$\Delta H = \Delta U = q_V$$

For solids and liquids, ΔV is very small; therefore, $p\Delta V$ is insignificant and $\Delta H = \Delta U$. For gases, ΔV and hence $p\Delta V$ have significant values, therefore at constant pressure, $\Delta H > \Delta U$. In chemical reaction involving gases, we have

$$\Delta V = \sum V_{\text{products}} - \sum V_{\text{reactants}} = n_B V_B - n_A V_A$$

where n_B is the stoichiometric coefficient of all products, n_A is the stoichiometric coefficient of all reactants, V_B is molar volume of products and V_A is the molar volume of reactants. For an ideal gas, $pV = nRT$. For one mole of gas,

$$V = \frac{RT}{p}$$

Substituting for V in the above equation, we get

$$\Delta V = n_B \frac{RT}{p} - n_A \frac{RT}{p}$$

or

$$p\Delta V = n_B RT - n_A RT = (n_B - n_A)RT = \Delta n_g RT$$

where $\Delta n = n_B - n_A$. Therefore,

$$\Delta H = \Delta U + p\Delta V = \Delta U + \Delta n_g RT \tag{7.12}$$

where Δn is the difference between stoichiometric coefficients of all gaseous products and all gaseous reactants. It is a number and does not represent moles. This equation is useful for calculating ΔH from ΔU.

Relationship between ΔU and ΔH

We have that

$$\Delta H = \Delta U + \Delta pV$$

Therefore,

$$\Delta H = \Delta V + (p_2 V_2 - p_1 V_1)$$

This equation is always applicable. Now let us consider the following cases:

1. For a substance undergoing physical or chemical change:

(a) For any ideal gas

$$\Delta H = \Delta U + \Delta(pV) = \Delta U + nR\Delta T$$

Therefore,

$$nC_p \Delta T = nC_V \Delta T + nR\Delta T$$

and

$$C_p = C_V + R$$

(b) For solids and liquids:

$$\Delta H = \Delta V + \Delta(pV)$$

Here, $\Delta(pV) \ll \Delta U$, therefore,

$$\Delta H \cong \Delta U$$

or

$$C_p \cong C_V$$

2. For chemical or phase change

(a) For reactions involving at least one gaseous component:

(i) If gases are assumed to be ideal gases

$$\Delta H = \Delta U + \Delta(pV) = \Delta U + \Delta(nRT) = \Delta U + \Delta n_g RT$$

as temperature is constant.

$$\Delta n_g = \Sigma n_{g(\text{products})} - \Sigma n_{g(\text{reactants})}$$

where n_g is number of gaseous moles.

(ii) If gases are assumed to be real gases

For example,

$$\underset{(p_1,V_1)}{CO_2} \rightarrow \underset{(p_2V_2)}{CO_2}$$

$$\Delta H = \Delta U + \Delta(pV)$$

or $$\Delta H = \Delta U + (p_2V_2 - p_1V_1)$$

(b) For reactions involving solids or liquids

$$\Delta(pV) \cong 0$$

$$\Delta H \cong \Delta U$$

Solved Example 7-11

Calculate the difference in ΔH and ΔU for combustion of methane at 25°C.

Solution

The combustion reaction of methane is given by

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

The enthalpy change in the reaction is expressed as

$$\Delta H = \Delta U + \Delta n_g RT$$

where Δn_g from the reaction is $\Delta n = 1 - (1+2) = -2$

Therefore, $\Delta H = \Delta U - 2RT$

Given that $T = 273 + 25 = 298$ K and $R = 8.314$ J K^{-1} mol^{-1}. Substituting these, we calculate the difference in ΔH and ΔU as

$$\Delta H - \Delta U = -2 \times 8.314 \times 298 = -4955.14\text{ J} = -4.95\text{ kJ}$$

Solved Example 7-12

Calculate the work done when 1 mol of zinc dissolves in hydrochloric acid at 273 K in **(a)** an open beaker; **(b)** a closed beaker at 300 K.

Solution

The reaction involved is

$$\underset{1\text{ mol}}{Zn(s)} + 2\,HCl\,(aq) \rightarrow ZnCl_2(aq) + \underset{1\text{ mol}}{H_2(g)}$$

(a) From one mole of zinc, the number of moles of H_2 gas evolved = 1 mol.

Hence, volume of hydrogen gas evolved = 22.4 L (at STP when p = L atm and T = 273 K). Work done is

$$w = -pdV = -1 \times 22.4\text{ L atm}$$

$$= -22.4 \times \frac{8.314}{0.082} = -2271.14\text{ J}$$

(b) For a closed system $p_{ext} = 0$, therefore, $w = 0$.

Solved Example 7-13

Consider 100 mL of a liquid contained in an isolated container at a pressure of 1 bar. The pressure is steeply increased to 100 bars. The volume of the liquid is decreased by 1 mL at this constant pressure. Find the ΔH and ΔU. **(IIT-JEE 2004)**

Solution

We know that at constant pressure conditions

$$\Delta H = \Delta U + \Delta(pV)$$

where $\Delta pV = p_2V_2 - p_1V_1$

Given that $p_1 = 1$ bar, $V_1 = 100$ mL, $p_2 = 100$ bar, $V_2 = 99$ mL. Substituting, we get

$$\Delta pV = 100 \times 99 - 1 \times 100 = 9800\text{ mL bar}$$
$$= 980\text{ J (as 1 L bar} = 180\text{ J)}$$

So, $\Delta H = 10 + 980 = 990$ J

Solved Example 7-14

For the reaction,

$$2CO + O_2 \rightarrow 2CO_2;\ \Delta H = -560\ \text{kJ}$$

Two moles of CO and one mole of O_2 are taken in a container of volume 1 L. They completely form two moles of CO_2, the gases deviated appreciably from ideal behavior. If the pressure in the vessel changes from 70 to 40 atm, find the magnitude (absolute value) of ΔU at 500 K. (1 L atm = 0.1 kJ) **(IIT-JEE 2006)**

Solution

From the definition of enthalpy, we have

$$\Delta H = \Delta U + \Delta(pV) = \Delta U + V\Delta p + p\Delta V$$

As at constant volume $\Delta V = 0$, so

$$\Delta U = \Delta H - V\Delta p = -560 + 1 \times 30 \times 0.1 = -557\ \text{kJ}$$

Solved Example 7-15

The reaction

$$2N_2O(g) \rightarrow 2N_2(g) + O_2(g)$$

has $\Delta H^{\circ} = -163.14$ kJ. What is the value of ΔU for the decomposition of 180 g of N_2O at 25°C? If we assume that ΔH does not change appreciably with temperature, what is ΔU for this same reaction at 200°C?

Solution

We know that $\quad \Delta H = \Delta U + \Delta n_g RT$

$$\Delta U = \Delta H - \Delta n_g RT$$

Given that $R = 8.314$ J K^{-1} mol^{-1}, $\Delta H = -163.14$ kJ mol^{-1},
$T = 25 + 273 = 298$ K, $\Delta n_g = 3 - 2 = 1$ mol.

For 180 g N_2O, first calculate the number of moles of N_2O and then how many kJ of energy will be released for that many moles of N_2O. Substituting the values, we have

$$\Delta U = -163.14\,\text{kJ} - (1\,\text{mol})(8.314 \times 310^{-3}\,\text{kJ}\,\text{mol}^{-1}\,\text{K}^{-1})(298\,\text{K})$$
$$= -165.62\ \text{kJ}$$

Number of mol N_2O = 180 g$\left(\dfrac{1\,\text{mol}\ N_2O}{44.02\ \text{g}\ N_2O}\right)$ = 4.09 mol N_2O

$$\text{Amount of energy released} = 4.09\ \text{mol}\ N_2O\left(\frac{-165.62\ \text{kJ}}{2\ \text{mol}\ N_2O}\right) = -338\ \text{kJ}$$

Now, for $T = 200°\text{C} = 200 + 273 = 473$ K,

$$\Delta U = -163.14\ \text{kJ} - (1\ \text{mol})(8.314 \times 10^{-3}\ \text{kJ mol}^{-1}\ \text{K}^{-1})(473\ \text{K})$$
$$= -163.14\ \text{kJ} - 3.93\ \text{kJ}$$

At 200°C, $\Delta U_{200°C} = -167.07$ kJ for 1 mol of N_2O

For 180 g N_2O, 4.09 mol N_2O reacts, so the amount of energy released at 200°C is

$$4.09\ \text{mol}\ N_2O\left(\frac{-167.07\ \text{kJ}}{2\ \text{mol}\ N_2O}\right) = -341\ \text{kJ}$$

7.7 | EXPANSION AND COMPRESSION OF AN IDEAL GAS

We shall use the first law of thermodynamics to calculate the changes in thermodynamics properties when an ideal gas undergoes the process of isothermal or adiabatic expansion (or compression) and determine the expressions for work done in each case. We will also use first law to determine heat changes in isobaric and isochoric processes. The pressure–volume work done by an ideal gas in these processes is depicted in Fig. 7.14(a). Figure 7.14(b) graphically represents expansion and compression of an ideal gas under isothermal and adiabatic conditions.

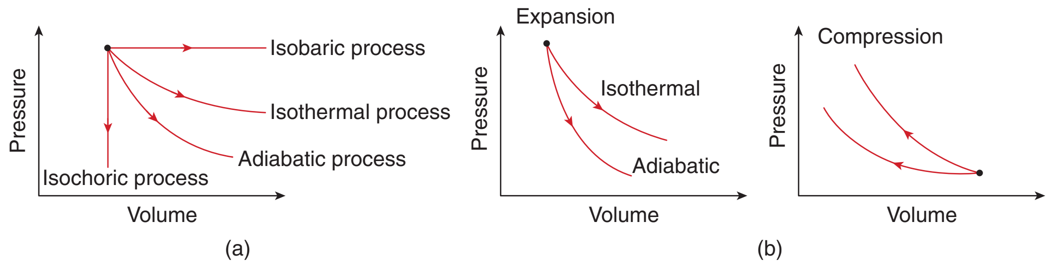


Figure 7.14 (a) Pressure–volume change in various processes. (b) Isothermal and adiabatic expansion and compression.

Isothermal Expansion or Compression

In an isothermal expansion or compression process, the temperature of the system remains constant throughout the expansion or compression process. Since for an ideal gas, U depends only on temperature [Joule's law, $((\partial U / \partial V)_T = 0)$] it follows that $\mathrm{d}U = 0$ or $\Delta U = 0$. Substituting this in the first law of thermodynamics, we get

$$\mathrm{d}q = -\mathrm{d}w \quad \text{or} \quad q = -w$$

Hence, in an isothermal expansion or compression process, heat is converted into work and vice versa. Thus if heat is supplied to the system (q positive), an equivalent amount of work is done by the system (w negative), and if some work is done on the system (w positive), the equivalent amount of heat is given out (q negative).

The enthalpy change of the system in isothermal expansion or compression is also zero as

$$\Delta H = \Delta(U + pV) = \Delta U + \Delta(pV) = \Delta U + \Delta(nRT) = \Delta U + nR(\Delta T) = 0 + 0 = 0$$

so, $\Delta U = \Delta H = 0$. The magnitude of w (or q) depends on how the expansion or compression process is carried out. For this, two different types of processes may be distinguished, namely, reversible and irreversible discussed in Section 7.1. The changes in q,w, ΔU and ΔH in these two types of processes are explained as follows.

Reversible Expansion or Compression Process

The expression for the work involved in an isothermal expansion from volume V_1 to V_2 has been derived in Section 7.3 as follows:

$$w = -\int_{V_1}^{V_2} \frac{nRT}{V}\,\mathrm{d}V$$

Since temperature remains constant in an isothermal process, we have

$$w = -nRT\int_{V_1}^{V_2} \frac{\mathrm{d}V}{V} = -nRT \ln\frac{V_2}{V_1}$$

In terms of pressure, we have

$$w = -nRT \ln\frac{p_1}{p_2}$$

Similarly, for an isothermal reversible compression, the expression can be derived as

$$q = -w = nRT \ln\frac{V_2}{V_1} = nRT \ln\frac{p_1}{p_2}$$

Irreversible Expansion or Compression Process

Two types of irreversible changes in volume may be distinguished, namely, expansion against a zero pressure (free expansion) and expansion or compression against a constant pressure (intermediate expansion or compression). The changes in q, w, ΔU and ΔH for these processes are given as follows:

Free expansion: Here $p_{\text{ext}} = 0$. Therefore, $w = \int \mathrm{d}w = -\int p_{\text{ext}}\,\mathrm{d}V = 0$. Thus, $q = -w = 0$ or $\Delta U = \Delta H = 0$.

Intermediate expansion or compression: Here, the work is done against a constant pressure. Therefore,

$$w = -\int_{V_1}^{V_2} p_{\text{ext}}\,\mathrm{d}V = -p_{\text{ext}}(V_2 - V_1)$$

Hence, in the present case we have

$$q = -w = p_{\text{ext}}(V_2 - V_1) \text{ and } \Delta U = \Delta H = 0$$

It may be mentioned here that the magnitude of work involved in an intermediate expansion process will be less than that involved in the reversible expansion. This is because for an irreversible process, p_{ext} is always less than the pressure of the gas (p) whereas both the quantities are nearly equal in a reversible process. The maximum work obtained from a system in isothermal expansion is when $p = p_{\text{ext}}$. When p_{ext} becomes greater than pressure of the gas, compression takes place.

The work involved in the intermediate compression process is larger than that involved in the reversible compression because $p_{ext} > p$ whereas these are nearly equal in a reversible process. Consequently, more heat will be released in case of intermediate compression.

Solved Example 7-16

One mole of an ideal gas at 300 K is heated at constant volume (V_1) until its temperature is doubled, then it is expanded isothermally till it reaches the original pressure. Finally, the gas is cooled at the constant pressure till system reached to the half of original volume ($V_1/2$). Determine the total work done (w) in calories. [Use ln 2 = 0.70, $R = 2$ cal K^{-1} mol^{-1}]

Solution

The temperature, pressure and volume conditions at each of the points A, B, C, D as shown in Fig. 7.15 are

$$A\,(p_1,V_1,T_1), B\,(2p_1,V_1,2T_1), C(p_1,2V_1,2T_1)_{I} D\left(2p_1,\frac{V_1}{2},\frac{T_1}{2}\right)$$

The total work done is given by $w_{\text{total}} = w_{AB} + w_{BC} + w_{CD}$

For isochoric change (AB), $w_{AB} = 0$.

For isothermal expansion (BC),

$$w_{BC} = -1 \times R \times 2T_1 \ln\left(\frac{2V}{V_1}\right) = -2 \times 2 \times 300 \times 0.7 = -840\,\text{cal}$$

For isobaric change (CD),

$$w_{CD} = -p_1\Delta V = -R\Delta T = -R\left[\frac{T_1}{2} - 2T_1\right]$$

$$= \frac{3}{2}RT_1 = \frac{3}{2} \times 2 \times 300 = 900\,\text{cal}$$

Therefore, $\quad w_{\text{total}} = -840 + 900 = 60$ cal

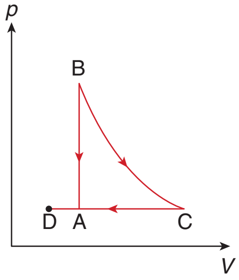


Figure 7.15

Solved Example 7-17

Calculate the maximum work done when 0.5 mol of a gas expands isothermally and reversibly from a volume of 2 L to 5 L at 27°C. What is the change in internal energy if 200 cal of heat is absorbed?

Solution

For a reversible isothermal expansion process, the work done is given by

$$w = -nRT \ln\frac{V_2}{V_1}$$

Given that $n = 0.5$ mol, $V_1 = 2$ L:, $V_2 = 5$ L, $T = 273 + 27 = 300$ K and $R = 1.987$ cal K^{-1} mol^{-1}. Substituting these values in the equation, we get

$$w_{\max} = 0.5 \times 1.987 \times 300 \times \ln\left(\frac{5}{2}\right)$$

$$= 0.5 \times 1.987 \times 300 \times 0.916 = 303.4\text{ cal}$$

According to first law of thermodynamics, for isothermal expansion

$$q = \Delta U + w$$

Given that $q = 200$ cal. Substituting values of q and w in the above equation, we get

$$\Delta U = 200 - 303.4 = -103.4\text{ cal}$$

Solved Example 7-18

1 mol of an ideal gas undergoes reversible isothermal expansion from an initial volume V_1 to a final volume, 10 V_1, and does 10 kJ of work. The initial pressure was 1×10^7 Pa. **(a)** Calculate V_1, **(b)** If there were 2 mol of gas, what must have been its temperature? **(IIT-JEE 2001)**

Solution

(a) For reversible isothermal expansion,

$$w = -2.303\, nR \log \frac{V_2}{V_1} = 2.303\, nR \log \frac{p_1}{p_2}$$

At constant $T, p_1V_1 = p_2V_2$, therefore,

$$1 \times 10^7 \times V_1 = p_2 \times 10V_1 \Rightarrow p_2 = 10^6 \text{ Pa}$$

Substituting value of pressure in expression for work, we have

$$-10 \times 10^{-3} = -2.303 \times 1 \times 8.314 \times T \log \frac{10^7}{10^6}$$

Solving, we get $T = 522.27$ K. Substituting in the gas equation $pV = nRT$,

$$1 \times 10^7 \times V_1 = 1 \times 8.314 \times 522.27$$

or $$V_1 = 4.34 \times 10^{-4} \text{ m}^3$$

(b) For 2 mol, $T = \dfrac{522.27}{2} = 261.13\,\text{K}$

Adiabatic Expansion or Compression

In adiabatic expansion or compression process, heat is neither allowed to enter nor leave the system. Therefore, $q = 0$. So, from the first law of thermodynamics, $\Delta U = q + w$, we have $\Delta U = w$.

If there is an expansion, w will be negative and, therefore, ΔU will be negative, that is, there will occur a decrease in the internal energy of the system and hence its temperature will fall. This amounts to the fact that the work is done by the system at the expense of internal energy.

If there is a compression, w will be positive and, therefore, ΔU will also be positive, that is, there will occur an increase in the internal energy and, hence, its temperature will rise. Here, the work is done by the surroundings on the system, which is stored as the internal energy.

Expression for q, w, ΔU and ΔH: We have seen above that $q = 0$ and $w = \Delta U$. The change in the energy can be calculated as follows:

Writing the differential of U, we get

$$\mathrm{d}U = \left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial U}{\partial T}\right)_T \mathrm{d}V$$

But for an ideal gas $(\partial U/\partial V)_T = 0$, so

$$\mathrm{d}U = \left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T$$

Hence, $\mathrm{d}U = n\mathrm{C}_{V,m}\,\mathrm{d}T$. For a finite change, we have

$$\Delta U = U_2 - U_1 = nC_{V,m}(T_2 - T_1) \tag{7.13}$$

Thus, we have $$w = \Delta U = nC_{V,m}(T_2 - T_1) \tag{7.14}$$

The change in enthalpy is given by

$$\begin{aligned}\Delta H &= \Delta(U + pV) = \Delta U + \Delta(pV) = \Delta U + nR\Delta T \\ &= nC_{V,m}(T_2 - T_1) + nR(T_2 - T_1) = n(C_{V,m} + R)(T_2 - T_1)\end{aligned}$$

or $$\Delta H = nC_{p,m}(T_2 - T_1) \tag{7.15}$$

Expression as given above is applicable to any type of adiabatic processes (reversible, irreversible, free). However, the final temperature will be different in each case and hence w, ΔU and ΔH will be different. We proceed now to calculate these quantities for the two types of expression or compression processes, namely, reversible and irreversible.

Adiabatic Reversible Expansion or Compression Process

The total work done is given by

$$w = \int \mathrm{d}w = -\int p_{\text{ext}}\,\mathrm{d}V = -\int p_{\text{int}}\,\mathrm{d}V$$

The integration in the above expression cannot be performed directly, because p_{int} is a function of both T and V and both variables are changing in an adiabatic expansion or compression process. However, if the final temperature is available, the value of q, w, ΔU and ΔH can be determined using Eqs. (7.13)–(7.15).

However, if the final temperature is not available but the final pressure or volume is available, the first step to calculate the final temperature from the expression which relates the initial and final temperatures to the respective volumes or pressures. Such an expression can be derived as follows:

1. **Relationship between *T* and *V*:** For an adiabatic process, the expression for the first law is

$$\mathrm{d}U = w$$

Since $\Delta U = nC_{V,m}\mathrm{d}T$ and $\mathrm{d}w = -p_{\text{ext}}\,\mathrm{d}V$, therefore, $nC_{V,m}\mathrm{d}T = -p_{\text{ext}}\,\mathrm{d}V$. For a reversible process,

$$p_{\text{ext}} = p_{\text{int}} \pm \mathrm{d}p \approx p_{\text{int}}$$

Thus, $nC_{V,m}\mathrm{d}T = -p_{\text{int}}\,\mathrm{d}V$. For an ideal gas, $p_{\text{int}} = (nRT/V)$ or

$$C_{V,m}\,\mathrm{d}T = -\frac{RT}{V}\mathrm{d}V$$

(Note that $C_{V,m}$ is molar heat capacity. The above equation will also be true for more than 1 mol of an ideal gas.) Thus, for a finite change, we have

$$\int_{T_1}^{T_2} C_{V,m}\frac{\mathrm{d}T}{T} = -\int_{V_1}^{V_2} R\frac{\mathrm{d}V}{V}$$

If $C_{V,m}$ is considered independent of temperature, then

$$C_{V,m}\ln\left(\frac{T_2}{T_1}\right) = -R\ln\left(\frac{V_2}{V_1}\right)$$

or

$$\ln\left(\frac{T_2}{T_1}\right)^{C_{V,m}} = \ln\left(\frac{V_2}{V_1}\right)^{-R}$$

or

$$\left(\frac{T_2}{T_1}\right)^{C_{V,m}} = \left(\frac{V_2}{V_1}\right)^{-R} = \left(\frac{V_1}{V_2}\right)^{R}$$

Therefore,

$$(T_2)^{C_{V,m}} \times (V_2)^R = (T_1)^{C_{V,m}} \times (V_1)^R$$

or

$$T^{C_{V,m}} \times V^R = \text{constant} \tag{7.16}$$

Eq. (7.16) can also be written as

$$TV^{R/C_{V,m}} = \text{constant} \quad \text{or} \quad T^{C_{V,m}/R}V = \text{constant}$$

Substituting $R = C_{p,m} - C_{V,m}$, we get

or

$$TV^{\gamma-1} = \text{constant} \tag{7.17}$$

where

$$\gamma = C_{p,m}/C_{V,m}$$

2. **Relationship between *T* and *p*:** Replacing V in Eq. (7.16) by RT/p, we get

$$T^{C_{p,m}}\left(\frac{RT}{p}\right)^R = \text{constant}$$

$$T^{C_{p,m}}p^{-R} = \text{constant}$$

The alternate forms of this expression are

$$Tp^{-R/C_{p,m}} = \text{constant or } T^{-C_{p,m}/R}\, p = \text{constant}$$

Substituting $R = C_{p,m} - C_{V,m}$, we get

$$Tp^{(1-\gamma)/\gamma} = \text{constant or } T^{\gamma(1-\gamma)}\, p = \text{constant} \tag{7.18}$$

3. **Relationship between p and V:** Replacing T in Eq. (7.18) by pV/R, we get

$$\left(\frac{pV}{R}\right)^{C_{V,m}} V^{R} = \text{constant}$$

or

$$p^{C_{V,m}} V^{C_{p,m}} = \text{constant}$$

The alternate form of this expression is

$$pV^{\gamma} = \text{constant} \tag{7.19}$$

where $\gamma = C_{p,m}/C_{V,m}$. After calculating final temperature from these expressions, we can use equation to calculate $q, w, \Delta U$ and ΔH.

Adiabatic Irreversible Expansion or Compression Process

Here again we consider two cases, namely, free expansion or and intermediate expansion or compression processes.

1. **Free expansion:** In a free expansion, we have $p_{\text{ext}}\,(V_2 - V_1)$. Thus, $\mathrm{d}w = -p_{\text{ext}}\,\mathrm{d}V = 0$. Now, according to this reaction, we have $\mathrm{d}U = 0$. Since, for an ideal gas, internal energy is a function of temperature, it follows that the temperature of the gas after expansion remains unchanged.

   Now, $$\mathrm{d}H = \mathrm{d}U + \mathrm{d}(pV) = \mathrm{d}U + \mathrm{d}(nRT) = \mathrm{d}U + nR\mathrm{d}T = 0 + 0 = 0$$

   For finite change we will have $w = 0$, $\Delta U = 0$, $\Delta T = 0$, $\Delta H = 0$. Comparing these changes in properties with those of the isothermal free expansion, we find that the adiabatic irreversible free expansion of an ideal gas is identical with the isothermal free expansion.

2. **Intermediate expansion or compression:** Here, the work is done against a constant external pressure and is given by

   $$w = -p_{\text{ext}}(V_2 - V_1)$$

   From the expression for first law for adiabatic process, we have

   $$w = \Delta U = -p_{\text{ext}}(V_2 - V_1)$$

   For an ideal gas, ΔU is given by $\quad \Delta U = nC_{V,m}\Delta T = nC_{V,m}(T_2 - T_1)$

   The expression for ΔH is $\quad \Delta H = nC_{p,m}\Delta T = nC_{p,m}(T_2 - T_1)$

   Eliminating ΔT from above equations, we get

   $$\Delta H = nC_{p,m}\frac{\Delta V}{nC_{V,m}} = \frac{nC_{p,m}}{nC_{V,m}}\Delta V = \gamma \Delta V$$

   This relation can be employed to calculate w and ΔV and from the given value of p_{ext}, V_2 and V_1. Knowing ΔU we can calculate ΔH by using above equation.

3. **Calculation of temperature:** In some expansion or compression processes, the value of p_{ext}, p_1, p_2 and T_1 are provided. In such a case, first of all we calculate the temperature of the gas after the expansion or compression. This can be done as follows:

   From the above equation we get

   $$nC_{V,m}(T_2 - T_1) = -p_{\text{ext}}(V_2 - V_1) = p_{\text{ext}}(V_1 - V_2)$$

Replacing V_1 and V_2 in terms of T and p, we get

$$nC_{V,m}(T_2 - T_1) = p_{\text{ext}}\left(\frac{nRT_1}{p_1} - \frac{nRT_2}{p_2}\right)$$

or

$$C_{V,m}(T_2 - T_1) = p_{\text{ext}}\left(\frac{RT_1}{p_1} - \frac{RT_2}{p_2}\right)$$

For a special cases, where $p_{\text{ext}} = p_2$ (the pressure of the gas after expansion), we have

$$C_{V,m}(T_2 - T_1) = p_2\left(\frac{RT_1}{p_1} - \frac{RT_2}{p_2}\right)$$

Rearranging this, we get

$$T_2 = T_1\left(\frac{C_{V,m} + Rp_2'p_1}{C_{p,m}}\right)$$

After calculating T_2 from this relation, if p_{ext} is not equal to p_2, we can calculate ΔU and ΔH from above equation, respectively.

Solved Example 7-19

A cylindrical container of volume 44.8 L is containing equal number of moles of an ideal monoatomic gas in two sections A and B separated by an adiabatic frictionless piston as shown in Fig. 7.16. The initial temperature and pressure of gas in both sections is 273 K and 1 atm. Now, the gas in section A is slowly heated till the volume of section B becomes (1/8)th of initial volume. Find the change in internal energy (ΔU) for section A in calories.

Given that R = 2 cal mol^{-1} K^{-1}; $C_{V,m}$ of monoatomic gas = (3/2) R. At STP, ideal gas occupies 22.4 L.

Solution

The initial volume in both the sections is 22.4 L. The gas in section B is compressed reversibly and adiabatically, therefore, using Eq. (7.17), we have

$$T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$$

$$T_2 = T_1\left(\frac{V_1}{V_2}\right)^{\gamma-1} = 27.3\times(8)^{2/3} = 4T_1$$

The final pressure in section A is given by

$$p_2 = p_1\left(\frac{V_1}{V_2}\right)\times\left(\frac{T_2}{T_1}\right) = 1\times8\times4 = 32 \text{ atm}$$

The final temperature in section A is given by

$$T_2 = T_1\left(\frac{p_2}{p_1}\right)\left(\frac{V_1}{V_2}\right) = 2703\times\left(\frac{32}{1}\right)\times1.875 = 1638\,\text{K}$$

Therefore, the change in internal energy of section A is given by

$$\Delta U_{\text{A}} = nC_{V,m}\Delta T = 0.1\times\frac{3}{2}R\times(1638 - 27.3) = 483.21\,\text{cal}$$

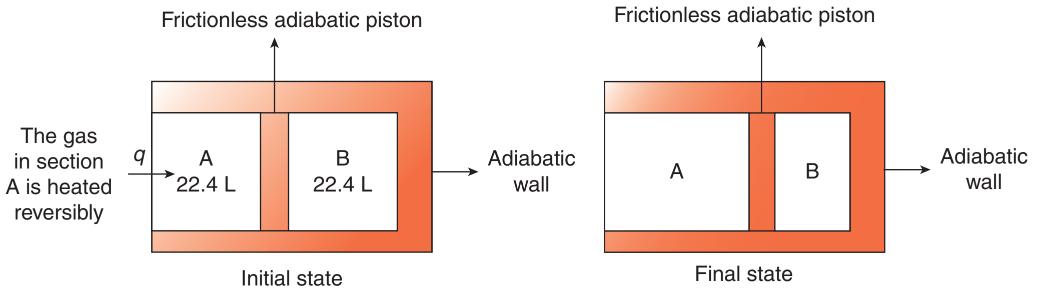

Frictionless adiabatic piston
The gas in section A is heated reversibly
q
A
22.4 L
B
22.4 L
Adiabatic wall
Initial state
Frictionless adiabatic piston
A
B
Adiabatic wall
Final state

Figure 7.16

Solved Example 7-20

Consider 2 mol of an ideal diatomic gas at 300 K and 0.507 MPa to be expanded adiabatically to a final pressure of 0.203 MPa against a constant pressure of 0.101 MPa. Calculate the final temperature.

Solution

For an adiabatic process $q = 0$. The work done is given by

$$w = -p_{\text{ext}}(V_2 - V_1) = -p_{\text{ext}}\left(\frac{nRT_2}{p_2} - \frac{nRT_1}{p_1}\right)$$

For an adiabatic process from first law, $\Delta U = w$. Therefore,

$$nC_V(T_2 - T_1) = p_{\text{ext}} nR\left(\frac{T_1}{p_1} - \frac{T_2}{p_2}\right) \quad (1)$$

For a diatomic molecule, $C_V = \frac{5}{2}R$. Substituting the expression of C_V in Eq. (1), we get

$$n\left(\frac{5}{2}R\right)(T_2 - T_1) = p_{\text{ext}} nR\left(\frac{T_1}{p_1} - \frac{T_2}{p_2}\right) \text{or} \frac{5}{2}(T_2 - T_1)$$

$$= p_{\text{ext}}\left(\frac{T_1}{p_1} - \frac{T_2}{p_1}\right)$$

Substituting the given values, we get

$$\frac{5}{2}(T_2 - T_1) = (0.101)\left[\frac{300}{0.507} - \frac{T_2}{0.203}\right]$$

Solving for T_2, we get $T_2 = 270$ K.

Solved Example 7-21

A sample of argon gas at 1 atm pressure and 27°C expands reversibly and adiabatically from 1.25 dm^3 to 2.50 dm^3. Calculate the enthalpy change in this process. $C_{V,\,m}$ for argon is 12.48 J K^{-1} mol^{-1} **(IIT-JEE 2000)**

Solution

For an adiabatic reversible expansion,

$$(T_2)^{C_{V,m}} \times (V_2)^R = (T_1)^{C_{V,m}} \times (V_1)^R$$

or

$$\ln\frac{T_1}{T_2} = \frac{R}{C_V}\ln\frac{V_2}{V_1}$$

On substituting values and solving, we get $T_2 = 188.5$ K. The number of moles of argon is given by

$$n = \frac{pV}{RT} = \frac{1 \times 1.25}{0.0821 \times 300} = 0.05\,\text{mol}$$

The enthalpy change is given by

$$\Delta H = nC_p\Delta T = 0.05 \times 20.8 \times (188.5 - 300) = 115.41 \text{ J}$$

Isobaric and Isochoric Processes

For an isobaric process, the pressure (p) remains constant, when volume changes from V_1 to V_2 at temperatures T_1 and T_2, the work done is given by

$$w = -p(V_2 - V_1) = -p\Delta V$$

The relation between heat absorbed at constant pressure and enthalpy change and internal energy change can be expressed in terms of molar heat capacity at constant pressure (C_p) and constant volume (C_V), respectively, by the following equations:

$$\Delta H = q_p = C_p(T_2 - T_1)$$

$$\Delta U = q_p + w = C_p(T_2 - T_1) - p(V_2 - V_1)$$

$$= C_p(T_2 - T_1) - R(T_2 - T_1) \quad (\text{as } pV = RT)$$

or

$$\Delta U = C_V(T_2 - T_1)$$

For an isochoric process, volume remains constant, therefore,

$$\mathrm{d}V = 0 \Rightarrow w = -p\mathrm{d}V = 0.$$

The relation between heat absorbed at constant volume and internal energy change and enthalpy change can be expressed in terms of molar heat capacity at constant volume and constant pressure, respectively, as

$$q_V = C_V(T_2 - T_1)$$

$$\Delta U = q_V + w = C_V(T_2 - T_1) \quad (\text{as } w = 0)$$

Therefore, $$\Delta H = \Delta U + \Delta(pV) = C_V(T_2 - T_1) + R(T_2 - T_1) \quad (\text{as } pV = RT)$$

or $$\Delta H = C_p(T_2 - T_1)$$

Solved Example 7-22

Calculate the enthalpy change when 36 g of water is heated from 27°C to 37°C at 1 atm pressure. The molar heat capacity of water (18.1 cal $\mathrm{K^{-1}\ mol^{-1}}$) remains constant in this temperature range.

Solution

In an isochoric process, enthalpy change is given by

$$\Delta H = nC_p(T_2 - T_1)$$

Given that $C_p = 18.1$ cal $\mathrm{K^{-1}\ mol^{-1}}$, $T_1 = 27 + 273 = 300$ K, $T_2 = 37 + 273 = 310$ K and $n = 36/18 = 2$ mol. Substituting values in the equation, we get

$$\Delta H = 2 \times 18.1 \times (310 - 300) = 36.2 \times 10 = 362\ \mathrm{cal\,mol^{-1}}$$

7.8 | JOULE–THOMSON EFFECT AND INVERSION TEMPERATURE

In an ideal gas, pV is constant at any given temperature at all pressures. However, when real gases are allowed to expand into vacuum or low-pressure region through a fine hole, the temperature of the gas is lowered. This effect is known as **Joule–Thomson effect**. The effect is attributed to the fact that work is done by the gas to overcome intermolecular force during expansion. This causes a decrease in internal energy, and hence a decrease in the temperature of the gas.

In the experimental setup for study of this effect, an insulated tube (adiabatic conditions) was fitted with a porous plug to allow gases to be kept at different pressures on either side. Volume V_1 of the gas at pressure p_1 was allowed to pass through the porous plug to a region where constant pressure is p_2 and volume of the gas became V_2 using two frictionless pistons at the end of the tube. Under such conditions, all gases, with the exception of hydrogen, experienced a cooling on expansion. Hydrogen was found to become warmer. The change in temperature was found to depend on initial temperature and pressure of gas. The process is isoenthalpic or conducted at constant enthalpy and this can be shown as follows

$$\text{Work done by the system} = -p_1V_1$$

$$\text{Work done on the system} = p_2V_2$$

From the first law of thermodynamics,

$$\Delta U = q + W = -(p_2V_2 - p_1V_1) = p_1V_1 - p_2V_2 \quad (\text{as } q = 0)$$

or $$U_2 - U_1 = p_1V_1 - p_2V_2$$

or $$U_2 + p_2V_2 = U_1 + p_1V_1$$

or $$H_2 = H_1$$

The rate of change of temperature with pressure at constant enthalpy is called Joule–Thomson coefficient and is denoted by μ.

$$\mu = \left(\frac{\partial T}{\partial p}\right)_H$$

A study of Joule–Thomson coefficient for a gas at various temperatures and pressures reveals that at any given temperature, m decreases with increase in pressure and becomes negative when the pressure is increased to a high value. This suggests that gases cool on adiabatic expansion at lower pressure and undergo a heating effect at higher pressure.

The pressure at which gases neither cool nor warm up on expansion, that is, $\mu = 0$ is called the **inversion point**. This point varies with temperature and for a given pressure, the temperature at which a gas on passage from higher to lower pressure through fine orifice does not undergo heating or cooling ($\mu = 0$) is known as **inversion temperature**. At constant pressure, each gas shows two inversion temperatures, the upper and lower one, between which it undergoes cooling on expansion and beyond which it undergoes heating. Most of the gases are below their upper inversion temperature at room temperature, and hence, cool on expansion. Hydrogen on the other hand, at room temperature, is above the upper inversion temperature and heats up on expansion.

In real gases, two cases may arise and these are discussed as follows:

1. **If attractive forces are dominant:** In this case work has to be done against the internal forces. Potential energy of gas increases and thus kinetic energy decreases. This is because total change in internal energy = 0. Therefore, temperature decreases or cooling effect is observed. Here,
   $\Delta U = 0, \Delta K.E.$ is negative and $\Delta P.E.$ is positive. Therefore, ΔT is negative and attractive forces dominate, so $T < \frac{2a}{Rb}$
   where inversion temperature $T_i = \frac{2a}{Rb}$
2. **If repulsive forces are dominant:** In this case, during expansion, internal forces do work in pushing the piston. Therefore, potential energy of gas decreases and kinetic energy increases. Temperature increases or heating effect is observed. Here, $\Delta U = 0$, $\Delta K.E.$ is positive and $\Delta P.E.$ is negative. Therefore, ΔT is positive and repulsive forces dominate, so

$$T_i > \frac{2a}{bR}$$

7.9 | CALORIMETRY

The amount of heat absorbed or released in a chemical reaction (heat of reaction) or a physical process can be measured by a technique called **calorimetry**. The heat associated with the process is determined by measuring the change in temperature it causes in its surroundings by using an apparatus called a **calorimeter**. The heat capacity of the calorimeter in known and it is immersed in a given volume of the liquid. The heat evolved in the process is calculated by measuring the temperature change caused by the process in the calorimeter.

Depending on the kind of reaction, the design of a calorimeter can be altered. The heats of reaction are measured under conditions of either constant volume or constant pressure. If the reaction is carried out in a closed, rigid container, the heat of the reaction can be measured under constant volume (q_V) conditions. On the other hand, if the reaction is carried out in an open container, constant pressure (q_p) conditions are maintained.

ΔU Measurement

The heat of reaction at constant volume is measured in a bomb calorimeter shown in Fig. 7.17. It is so called because the steel container in which the reaction is carried out resembles a small bomb. The container is immersed in a water bath and a constant temperature is maintained till the moment reaction occurs by adding or removing heat from water. The calorimeter is generally used to measure the heat of combustion of a combustible substance by burning it in pure oxygen supplied to the steel container.

The volume of the reaction chamber is fixed, so $p\Delta V$ must equal zero for reactions. The walls of the container are rigid, so the change in volume, ΔV, is zero when the reaction occurs. The heat is thus absorbed at constant volume. As

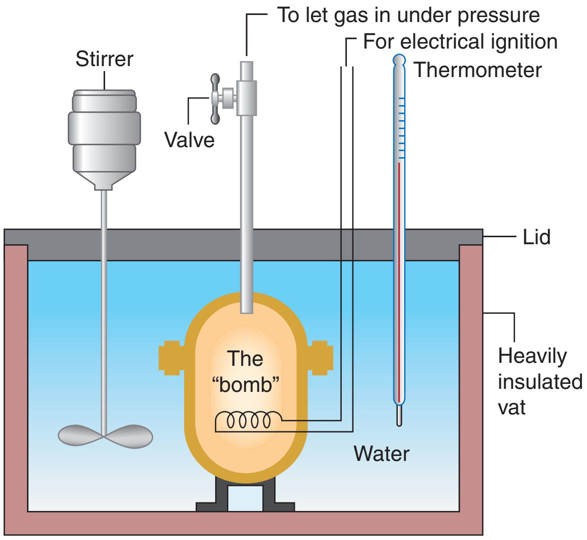


Figure 7.17 Bomb calorimeter.

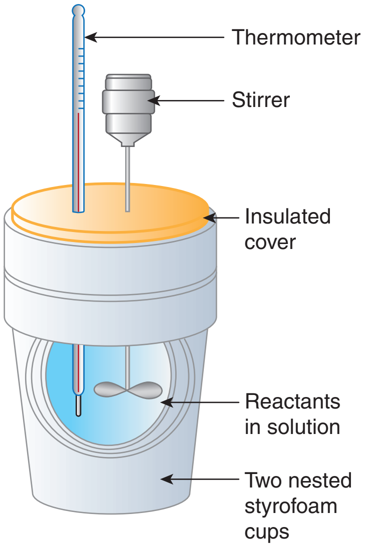


Figure 7.18 Calorimeter.

$p\Delta V$ is zero, and no expansion work is done, so w in equation $\Delta U = q_V + w$ is also zero. Therefore, the heat of reaction measured in a bomb calorimeter is the **heat of reaction at constant volume, q_V**, and corresponds to ΔU.

$$\Delta U = q_V$$

ΔH Measurement

An apparatus to measure heat change at constant pressure is a calorimeter, made of two nested and capped cups made of styrofoam (which is a very good insulator) (Fig. 7.18). This calorimeter is also known as coffee cup calorimeter. The change in temperature is fast and can be measured very easily. We can use the relation to find the heat of reaction at constant pressure, if we have determined the heat capacity of the calorimeter and its contents before the reaction.

$$q_p = C_p\Delta T = \Delta H$$

The cup made up of styrofoam and the thermometer absorbs negligible amount of heat that can be ignored.

Solved Example 7-23

When 1 g of olive oil was completely burned in pure oxygen in a bomb calorimeter, the temperature of the water bath increased from 22°C to 26.049°C. How many dietary calories are present in olive oil, per gram? The heat capacity of the calorimeter is 9.032 kJ°C^{-1}.
Assume that olive oil is almost pure glyceryl trioleate, $C_{57}H_{104}O_6$. The equation for its combustion is

$$C_{57}H_{104}O_6 + 80O_2 \rightarrow 57CO_2 + 52H_2O$$

Also calculate the change in internal energy, ΔU, for the combustion of one mole of glyceryl trioleate.

Solution

First, let us compute the heat absorbed by the calorimeter when 1 g of olive oil is burned:

$$q_{\text{Calorimeter}} = C\Delta T = (9.032\,\text{kJ°C}^{-1}) \times (26.049\,°\text{C} - 22.000\,°\text{C})$$
$$= -36.57\ \text{kJ}$$

Changing the algebraic sign gives the heat of combustion of 1 g of olive oil, $q_V = 36.57$ kJ. We convert to kilocalories (kcal), which are equivalent to dietary calories (cal):

$$\frac{-36.57 \times 1 \times 1}{1 \times 4.184 \times 1} = -8.740\ \text{cal g}^{-1}\ \text{oil}$$

Thus, 8.740 dietary calories are released when 1 g of olive oil is burned. For calculating the internal energy change, we will convert the heat produced per gram to the heat produced per mole, using the molar mass of $C_{57}H_{104}O_6$, 885.39 g mol^{-1}:

$$\frac{-36.57 \times 885.39}{1 \times 1} = -3.238 \times 10^4\ \text{kJ mol}^{-1}$$

Since this is heat at constant volume, we have

$$\Delta U = q_V = -3.238 \times 10^4\ \text{kJ}$$

for the combustion of 1 mol of $C_{57}H_{104}O_6$.

Solved Example 7-24

A 1.5 g sample of carbon is burned in a bomb calorimeter which has a heat capacity of 8.930 kJ°C^{-1}. The temperature of the water jacket rises from 20°C to 25.51°C. What is ΔU for the combustion of 1 mol of carbon?

Solution

Heat absorbed by calorimeter $= (25.51 - 20.00)\left(\frac{8.930}{1}\right) =$ 49.2 kJ

The number of moles of carbon, $n = 1.50 \times \left(\frac{1}{12.01}\right) =$ 0.125 mol

The internal energy per mole of carbon is $\Delta U = \frac{49.2}{0.125} =$ 394 kJ mol^{-1}

Solved Example 7-25

The reaction of hydrochloric acid and sodium hydroxide is very rapid and exothermic. The equation is

$$\text{HCl(aq)} + \text{NaOH(aq)} \rightarrow \text{NaCl(aq)} + \text{H}_2\text{O}$$

In one experiment, a student placed 50 mL of 1 M HCl at 25.5°C in a coffee cup calorimeter. To this was added 50 mL of 1 M NaOH solution also at 25.5°C. The mixture was stirred, and the temperature quickly increased to a maximum of 32.2°C. What is ΔH expressed in kJ per mole of HCl? Because the solutions are relatively dilute, we can assume that their specific heats are close to that of water, 4.18 J g^{-1}°C^{-1}. The density of 1 M HCl is 1.02 g mL^{-1} and that of 1 M NaOH is 1.04 g mL^{-1}.

Solution

For the HCl solution, the density is 1.02 g mL^{-1} and we have

$$\text{Mass (HCl)} = \frac{1.02}{1} \times 50 = 51 \text{ g}$$

Similarly, for the NaOH solution, the density is 1.04 g mL^{-1} and mass is $\frac{1.04}{1} \times 50 = 52$ g

The mass of the final solution is, thus, the sum 103 g. The reaction changes the system's temperature by $(T_f - T_i)$, so

$$\Delta T = 32.2 - 25.5 = 6.7\,°\text{C}$$

Now we can calculate the heat absorbed by the solution using the following relation:

$$\begin{aligned}\text{Heat absorbed by the solution} &= \text{Mass} \times \text{Specific heat} \times \Delta T\\ &= 103 \times 4.18 \times 6.7\\ &= 2.9 \times 10^3 = 2.9 \text{ kJ}\end{aligned}$$

Changing the sign gives the heat evolved by the reaction, $q_p = -2.9$ kJ. For calculating ΔH in kilojoules per mole of HCl, we calculate the number of moles of HCl in 50 mL of HCl solution (0.05 L) as

$$0.05 \times \frac{1}{1} = 0.05 \text{ mol HCl}$$

The neutralization of 0.0500 mol of acid has $q_p = -2.9$ kJ. To calculate the heat released per mole, ΔH, we simply take the ratio of joules to moles.

$$\Delta H \text{ per mol of HCl} = \frac{-2.9}{0.05} = -58 \text{ kJ mol}^{-1} \text{ HCl}$$

Thus, ΔH for neutralizing HCl by NaOH is -58 kJ mol^{-1} HCl.

Solved Example 7-26

When pure sulphuric acid dissolves in water, large amount of heat is given off. To measure it, 175 g of water was placed in a coffee cup calorimeter and chilled to 10°C. Then 4.9 g of sulphuric acid (H_2SO_4), also at 10°C, was added, and the mixture was quickly stirred with a thermometer. The temperature rose rapidly to 14.9°C. Since the solution is dilute, assume that the value of the specific heat of the solution is 4.184 J g^{-1}°C^{-1} (same as that of water), and that the solution absorbs all the heat evolved. Calculate the heat evolved in kilojoules by the formation of this solution. Also calculate the heat evolved per mole of sulphuric acid.

Solution

The heat released in the process is given by

$$\begin{aligned}q &= \text{Mass} \times \text{Specific heat} \times \Delta T\\ &= (175 + 4.9) \times 4.184 \times (14.9 - 10)\\ &= 3.7 \times 10^3 \text{ J} = 3.7 \text{ kJ}\end{aligned}$$

This should then be converted to a value representing kJ per mole of reactant, remembering that the sign of ΔH is to be negative, since the process releases heat energy to surroundings. The number of moles of sulphuric acid is:

$$n = 4.90 \times \left(\frac{1}{98.06}\right) = 5.00 \times 10^{-2}\ \text{mol}$$

and the enthalpy change per mole is given by

$$\Delta H = \frac{3.7}{0.05} = 74\ \text{kJ mol}^{-1}$$

7.10 | THERMOCHEMISTRY

The study of energy or heat changes accompanying a chemical reaction or a physical change is called **thermochemistry**. A chemical reaction or physical transformation such as phase change is accompanied by evolution or absorption of heat, that is, to say that all physical or chemical changes cause conversion of chemical energy to heat energy or vice versa. Reactions which involve absorption of heat are called **endothermic reactions**, whereas reactions involving release of heat are called **exothermic reactions**.

Enthalpy Changes During Phase Transformations

Transition from one phase to the other involves energy changes, for example, ice melts on heating. The phase transformations occur at constant (atmospheric) pressure and constant temperature, and thus, we have specific melting or boiling points of substances. The enthalpy changes accompanying different phase changes are described as follows.

1. **Heat (enthalpy) of fusion:** It is the enthalpy change of the system when one mole of a solid substance is converted into the liquid state at its melting point. For example, when ice melts at 0°C, the heat of fusion is $\Delta H^{\circ}_{\text{fus}} = +6.00$ kJ mol^{-1}.

$$H_2O(s) \rightarrow H_2O(l)$$

2. **Heat (enthalpy) of vaporization:** It is the enthalpy change of the system when one mole of liquid is converted into vapor or gaseous state at its boiling point. For example, when water boils to form steam, the heat of vaporization is $\Delta H^{\circ}_{\text{vap}} = +40.79$ kJ mol^{-1}.

$$H_2O(l) \rightarrow H_2O(vap)$$

3. **Heat (enthalpy) of sublimation:** It is the enthalpy change when one mole of a solid is directly converted into the gaseous form at a temperature below its melting point. For example, the heat of sublimation for iodine is $\Delta H^{\circ}_{\text{sub}} = +61.1$ kJ mol^{-1}.

$$I_2(s) \rightarrow I_2(g)$$

Some characteristic features of enthalpy changes accompanying phase transformations can be listed as follows:

1. When a substance is heated, its temperature rises and it eventually undergoes a phase transformation. The heat is required to overcome the intermolecular interactions which are in the order solid > liquid > gas.
2. The phase transition takes place at constant temperature under constant (atmospheric) pressure.
3. The phase transformation represents equilibrium between two physical states.
4. The magnitude of enthalpy change depends on the nature of intermolecular forces in the substance. For example, substances in which molecules are held together by van der Waals (London) forces (e.g., methane) have lower enthalpies for vaporization; those with dipole–dipole interactions (e.g., acetone) have higher values and those with inter-molecular and intra-molecular hydrogen bonding (e.g., water) even higher.

The standard enthalpies of vaporization of some substances are given in Table 7.2 along with types of attractive forces.

Table 7.2 Some typical heats of vaporization

Substance	ΔH_{vap}(kJ mol^{-1})	Type of attractive force
H_2O	+43.9	Hydrogen bonding and London
NH_3	+21.7	Hydrogen bonding and London
HCl	+15.6	Dipole–dipole and London
SO_2	+24.3	Dipole–dipole and London
F_2	+5.9	London
Cl_2	+10.0	London
Br_2	+15.0	London
I_2	+22.0	London
CH_4	+8.16	London
C_2H_6	+15.1	London
C_3H_8	+16.9	London
C_6H_{14}	+30.1	London

Enthalpy of Formation

It is the enthalpy change of a system when one mole of compound is formed from its constituent elements. It is represented as $\Delta_f H$ or ΔH_f. For example, for the formation of iron sulphide from iron and sulphur, the heat of formation is $\Delta H_f = -24.0$ kcal.

$$\text{Fe(s)} + \text{S(s)} \rightarrow \text{FeS(s)}$$

Standard heat of formation is the enthalpy change when one mole of a compound is formed from its constituent elements, at 298 K and one atmospheric pressure. It is represented as ΔH_f°.

Standard enthalpies of formation for a variety of substances are given in Table 7.3. Notice in particular that *all values of* $\Delta_f H^\circ$ *for the elements in their standard states are zero*. Forming an element *from itself*, of course, does not yield a change in enthalpy. In most tables, values of $\Delta_f H^\circ$ for the elements are not included for this reason.

Table 7.3 Standard enthalpies of formation of typical substances

Substance	$\Delta_f H^\circ$ (kJ mol^{-1})	Substance	$\Delta_f H^\circ$ (kJ mol^{-1})
Ag(s)	0	H_2O_2(l)	–187.6
AgBr(s)	–100.4	HBr(g)	–36
AgCl(s)	–127.0	HCl(g)	–92.30
Al(s)	0	HI(g)	26.6
Al_2O_3(s)	–1669.8	HNO_3(l)	–173.2
C(s, graphite)	0	H_2SO_4(l)	–811.32
CO(g)	–110.5	$HC_2H_3O_2$(l)	–487.0
CO_2(g)	–393.5	Hg(l)	0
CH_4(g)	–74.848	Hg(g)	60.84
CH_3Cl(g)	–82.0	I_2(s)	0
CH_3I(g)	14.2	K(s)	0
CH_3OH(l)	–238.6	KCl(s)	–435.89
$CO(NH_2)_2$(s) (urea)	–333.19	K_2SO_4(s)	–1433.7
$CO(NH_2)_2$(aq)	–391.2	N_2(g)	0
C_2H_2(g)	226.75	NH_3(g)	–46.19

(Continued)

Table 7.3 (Continued)

Substance	$\Delta_f H^\circ$ (kJ mol^{-1})	Substance	$\Delta_f H^\circ$ (kJ mol^{-1})
C_2H_4(g)	52.284	NH_4Cl(s)	–315.4
C_2H_6(g)	–84.667	NO(g)	90.37
C_2H_5OH(l)	–277.63	NO_2(g)	33.8
Ca(s)	0	N_2O(g)	81.57
$CaBr_2$(s)	–682.8	N_2O_4(g)	9.67
$CaCO_3$(s)	–1207	N_2O_5(g)	11
$CaCl_2$(s)	–795.0	Na(s)	0
CaO(s)	–635.5	$NaHCO_3$(s)	–947.7
$Ca(OH)_2$(s)	–986.59	Na_2CO_3(s)	–1131
$CaSO_4$(s)	–1432.7	NaCl(s)	–411.0
$CaSO_4{\cdot}H_2O$(s)	–1575.2	NaOH(s)	–426.8
$CaSO_4{\cdot}2H_2O$(s)	–2021.1	Na_2SO_4(s)	–1384.5
Cl_2(g)	0	O_2(g)	0
Fe(s)	0	Pb(s)	0
Fe_2O_3(s)	–822.2	PbO(s)	–219.2
H_2(g)	0	S(s)	0
H_2O(g)	–241.8	SO_2(g)	–296.9
H_2O(l)	–285.9	SO_3(g)	–395.2

Enthalpy of Reaction

The enthalpy of reaction is the amount of heat absorbed or evolved in a particular reaction, when the number of moles of reactants as represented by the balanced chemical equation change completely into the products. It is the difference between the heat content or enthalpies of the products and the reactants. It is represented as

$$\Delta H = \text{Heat of products} - \text{Heat of reactants.}$$

$$\Delta_r H = \text{Enthalpies of formation of products} - \text{Enthalpies of formation of reactants}$$

or

$$\Delta_r H = \sum_i a_i H_{\text{f, products}} - \sum_i b_i H_{\text{f, reactants}} \tag{7.20}$$

The summation sign indicates that the enthalpies for all reactants and products are summed and a_i and b_i indicate the stoichiometric coefficients of the reactants and products in a balanced chemical equation. For example, consider the reaction for preparation of ammonia

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

The molar enthalpy for formation of ammonia is given by molar enthalpies of participating species.

$$\Delta_r H = 2H_m(NH_3, g) - H_m(N_2, g) + 3H_m(H_2, g)$$

The enthalpy of reaction varies with the temperature. When enthalpy of products is more than that of reactants, ΔH is positive. Heat will be absorbed during such a reaction, and the reaction will be endothermic. On the other hand, if the enthalpy of reactants is more than the enthalpy of products, ΔH is negative, heat will be evolved in such a reaction and the reaction will be exothermic. For a chemical reaction, the enthalpy change $\Delta_r H$ will be negative for an exothermic reaction as the system loses heat to the surroundings and positive for an endothermic reaction because heat is absorbed by the system.

The heat change for a reaction taking place at standard conditions of temperature and pressure, that is, 298 K and 1 bar, is called **standard heat of reaction** or **standard enthalpy change** and is denoted by ΔH°. All the participating substances (reactants and products) are in their standard states. For example, for the reaction $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$, $\Delta H^\circ = -284.5$ kJ mol^{-1}.

Factor Affecting Enthalpy of Reaction

The enthalpy of reaction would depend on a number of factors listed as follows:

1. **The physical state of reactants and products:** It is important to specify the physical state of reactants and products in the reaction, because the heat of reaction will vary when the reactants are in different physical states. The heat of reaction between reactants in gaseous state will be different from when they are in liquid or solid state. Stating the temperature and pressure conditions at which the rate of reaction is measured is also important because it will affect the physical state of reactants and products.
2. **Temperature:** The heat of reaction varies with the temperature at which it is determined and the variation in the heat of reaction with temperature is given by **Kirchhoff's equation**. Using this relation, we can find the enthalpy of a reaction at any temperature, if the value at some other temperature is given, along with the values of heat capacities for the reactants and products. For example, consider a reaction:

$$A + B \rightarrow C + D$$

Enthalpy of the reaction is

$$\Delta H = (H_C + H_D) - (H_A + H_B)$$

We can show that for a reaction taking place at constant pressure,

$$\frac{d\Delta H}{dT} = \Delta C_p \tag{7.21}$$

where ΔC_p is the difference in the heat capacities of products and reactants at constant pressure. Rearranging Eq. (7.21), we get

$$d(\Delta H) = \Delta C_p \, dT$$

Integrating between the two values of enthalpy H_1 and H_2 at two different temperatures T_1 and T_2, we get

$$\int_{H_1}^{H_2} d(\Delta H) = \int_{T_1}^{T_2} \Delta C_p \, dT$$

$$(\Delta H_2 - \Delta H_1) = \Delta C_p (T_2 - T_1) \tag{7.22}$$

Similarly, for reactions at constant volume, the relation can be expressed for change in internal energy with temperature as

$$(\Delta U_2 - \Delta U_1) = \Delta C_V (T_2 - T_1) \tag{7.23}$$

We have

$$\int_{H_2}^{H_1} d(\Delta H) = \int_{T_1}^{T_2} \Delta C_p \, dT$$

Case 1: If ΔC_p is constant, then

$$\Delta H_2 - \Delta H_1 = \Delta C_p (\Delta T)$$

Case 2: If $\Delta C_p = f(T)$, then

$$\Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} f(T)\, dT$$

3. **Quantity of reactants:** The enthalpy of reaction increases with increase in number of moles of reactants. It is doubled when number of moles of reactants is doubled.
4. **Allotropic forms of reactants:** The enthalpy of reaction is different for different allotropic forms of reactants. For example, the enthalpy of formation of carbon dioxide from graphite and diamond (both allotropic forms of carbon) is different.

$$\underset{\text{Graphite}}{C(s)} + O_2(g) \rightarrow CO_2(g); \Delta H = -393.4 \text{ kJ}$$

$$\underset{\text{Diamond}}{C(s)} + O_2(g) \rightarrow CO_2(g); \Delta H = -395.4 \text{ kJ}$$

Relation between Enthalpy of Formation and Enthalpy of Reaction

Consider the following reactions with their standard heats of formation:

1. The standard enthalpy change when 1 mol of water is formed by combination of hydrogen and oxygen in their reference states is given by

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(l); \quad \Delta_f H^\circ (\text{at } 298 \text{ K, } 1 \text{ bar}) = -285.9 \text{ kJ mol}^{-1}$$

2. The standard enthalpy change when 1 mol of carbon dioxide is formed by combination of carbon and oxygen in their standard states is given by

$$C(\text{s, graphite}) + O_2(g) \rightarrow CO_2(g); \quad \Delta_f H^\circ (\text{at } 298 \text{ K, } 1 \text{ bar}) = -393.5 \text{ kJ mol}^{-1}$$

3. The standard enthalpy of formation when methane is formed from its constituent elements in their standard states is given by

$$C(\text{s, graphite}) + 2H_2(g) \rightarrow CH_4(g); \quad \Delta_f H^\circ (\text{at } 298 \text{ K, } 1 \text{ bar}) = -74.84 \text{ kJ mol}^{-1}$$

In the above examples, the heat of reactions ($\Delta_r H$) for water and carbon dioxide are –286 and –393.5 kJ mol^{-1}, respectively. Thus, molar enthalpy of formation can be considered as a special case of heat of reaction in which 1 mol of a compound is formed from its constituent elements. However, if we consider the formation of calcium carbonate from quick lime and carbon dioxide

$$CaO(s) + CO_2(g) \rightarrow CaCO_3(s); \quad \Delta_r H^\circ (\text{at } 298 \text{ K, } 1 \text{ bar}) = -178.3 \text{ kJ mol}^{-1}$$

The heat of reaction in this case does not correspond to heat of formation of $CaCO_3$ because it is not being formed by its constituent elements as required by the definition. Similarly, consider the formation of ammonia from nitrogen and hydrogen

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g); \quad \Delta_r H^\circ (\text{at } 298 \text{ K, } 1 \text{ bar}) = -92.38 \text{ kJ mol}^{-1}$$

The heat of reaction, in this case, is also not equal to the heat of formation, even though ammonia is formed from its constituent elements. The reaction involves formation of 2 mol of ammonia, whereas by definition, heat of formation corresponds to enthalpy of formation of 1 mol of substance. However, we have from Table 7.3 that $\Delta_f H^\circ (\text{at } 298 \text{ K, } 1 \text{ bar}) = -46.19 \text{ kJ mol}^{-1}$. Therefore, at 298 K and 1 bar

$$\Delta_r H^\circ = 2\Delta H_f^\circ$$

Thus, in a reaction if a number of moles (n) of a substance are formed from its constituent elements, then

$$\Delta_r H^\circ = n\Delta H_f^\circ$$

The expression for enthalpy of formation can be obtained by dividing the balanced chemical equation by n.

Solved Example 7-27

The heat evolved on combustion of 1 g starch $(C_6H_{10}O_5)_n$ into CO_2 and $H_2O(l)$ is 17.49 kJ g^{-1}. Compute the enthalpy of formation of 1 g starch. Given ΔH_f° of $H_2O(l) = -285.85$ kJ mol^{-1}, ΔH_f° of $CO_2 = -293.7$ kJ mol^{-1}.

Solution

Given that

$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O(l); \ \Delta H_f^\circ = -285.85 \text{kJ mol}^{-1}$$

$$C + O_2 \rightarrow CO_2(l) \qquad \Delta H_f^{o} = -293.7\ \text{kJ mol}^{-1}$$

Since the heat evolved on combustion of 1 g starch is 17.49 kJ, the heat evolved on combustion of $162n$ g starch is $17.49 \times 162n = 2833.38n$ kJ mol^{-1}.

The molecular weight of starch $(C_6H_{10}O_5)_n$ = $162n$. Therefore, for the reaction

$$(C_6H_{10}O_5)_n + 6n\ O_2 \rightarrow 6n\ CO_2 + 5n\ H_2O;$$
$$\Delta H_f^{o} = -2833.38n\ \text{kJ mol}^{-1} \qquad (1)$$

For the reaction

$$5n\ H_2 + \tfrac{5n}{2}O_2 + 6n\ C + 6n\ O_2 \rightarrow 5n\ H_2O + 6n\ CO_2$$

The heat of reaction can be calculated from the given heat of formation of H_2O and CO_2 as

$$\Delta_r H = 5n\Delta H_f(H_2O) + 6n\Delta H_f(CO_2)$$

$$\Delta_r H = 5n \times (-285.85) + 6n(-293.7)$$
$$= 3191.45n\ \text{kJ mol}^{-1} \qquad (2)$$

The heat of formation of starch can be calculated by subtracting Eq. (1) from Eq. (2)

$$6n\ C + 5n\ H_2 + \tfrac{5n}{2}O_2 + \rightarrow (C_6H_{10}O_5)_n;\ \Delta H_f^{o} = -358.07n\ \text{kJ mol}^{-1}$$

Heat of formation of 1 g of starch

$$= -\frac{358.07n}{162n} = -2.21\,\text{kJ mol}^{-1}$$

Solved Example 7-28

Estimate the maximum possible temperature of a Bunsen burner flame. Assume that the gas is pure methane and that it is premixed with sufficient air to permit complete combustion. Given that

$CH_4(g) + 2O_2(g) \rightarrow 2H_2O(l) + CO_2(g)\ \Delta_r H^{\circ}_{298\,K} = -890.36$ kJ mol^{-1}

$H_2O(l) \rightarrow H_2O(g)\ \Delta_r H^{\circ}_{298\,K} = 44.02$ kJ mol^{-1}

C_p of $CO_2(g) = 37.11$ J K^{-1} mol^{-1}

C_p of $H_2O(g) = 33.58$ J K^{-1} mol^{-1}

Solution

To calculate the temperature of the flame we have to consider adiabatic conditions where there is no loss of heat from the system. The rise in temperature can be calculated by considering the reaction to take place in the following two steps, both at constant pressure.

Step 1: Reactants $(T_0, p) \rightarrow$ Products $(T_0, p)\ \Delta_r H_{T_0}$

Step 2: Products $(T_0, p) \rightarrow$ Products $(T_f, p)\ \Delta_r H_2$

$$\Delta_r H_2 = \int_{T_0}^{T_f} C_p\,(\text{products})\,dT$$

Since the overall reaction is the sum of the above two steps, that is, the net heat change is given by

$$\Delta_r H = \Delta_r H_{T_0} + \Delta_r H_2$$

Since the reaction is considered to be adiabatic, therefore,

$$\Delta_r H = 0.$$

Thus, $\quad \Delta_r H_{T_0} + \Delta_r H_2 = 0$

or $\quad \Delta_r H_2 = -\Delta_r H_{T_0}$

or $\quad -\Delta_r H_{T_0} = \int_{T_0}^{T_f} C_p\,dT$

If C_p is independent of temperature, then

$$-\Delta_r H_{T_0} = C_p(T_f - T_0) \quad \text{or} \quad T_f = -\frac{\Delta_r H_{T_0}}{C_p} + T_0 \qquad (1)$$

At 298 K, we have

$$\Delta_r H^{o}_{298\,K} = -890.36 + 44.02 \times 2 = -802.32\ \text{kJ mol}^{-1}$$

For the reaction,

$$CH_4(g) + 2O_2(g) \rightarrow 2H_2O(g) + CO_2(g)$$

C_p of products $= 37.11 + 2 \times 33.58 = 104.27$ J K^{-1} mol^{-1}

Substituting values in Eq. (1), we get

$$T_f = \frac{802.32}{104.23} \times 10^3 + 298 = 7995.59\,\text{K} \simeq 8000\,\text{K}$$

7.11 | THERMOCHEMICAL EQUATIONS

A balanced chemical equation that indicates the enthalpy change accompanying the reaction is called a **thermochemical equation**. It gives the physical states of the reactants and products, and *its* ΔH^{o} *value is true only when the coefficients of the reactants and products are taken to mean moles of the corresponding substances*. For example, the following thermochemical equation is for the exothermic reaction of hydrogen and oxygen that produces water.

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l) \quad \Delta H^{o} = -571.8\ \text{kJ mol}^{-1}$$

These equations can be multiplied, added or subtracted like ordinary algebraic equations. The corresponding enthalpies of reactions are also mathematically manipulated in the same way so as to give the overall enthalpy of reaction under consideration.

> **Note:** We must write down physical states for all reactants and products in thermochemical equations. The combustion of 1 mol of methane, for example, has different values of ΔH° if the water produced is in its liquid or gaseous state.

$$\mathrm{CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)}; \quad \Delta H^{\circ} = -890.5\ \mathrm{kJ\ mol^{-1}}$$
$$\mathrm{CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)}; \quad \Delta H^{\circ} = -802.3\ \mathrm{kJ\ mol^{-1}}$$

(The difference in ΔH° values for these two reactions is the amount of energy that would be released by the physical change of 2 mol of water vapor at 25°C to 2 mol of liquid water at 25°C.)

Rules for Manipulating Thermochemical Equations

1. If all the coefficients of an equation are multiplied or divided by the same factor, the value of ΔH° must likewise be multiplied or divided by that factor. To illustrate this, let us use the reaction between gaseous nitrogen and hydrogen that produces gaseous ammonia.

$$\mathrm{N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)}; \quad \Delta H^{\circ} = -92.38\ \mathrm{kJ\ mol^{-1}}$$

When specifically 1 mol of N_2 and 3.000 mol of H_2 react to form 2 mol of NH_3 at 25°C and 1 bar, the reaction releases 92.38 kJ mol^{-1}. If we were to make twice as much or 4 mol of NH_3 (from 2.000 mol of N_2 and 6 mol of H_2), then twice as much heat (184.8 kJ mol^{-1}) would be released. On the other hand, if only 0.5000 mol of N_2 and 1.500 mol of H_2 were to react to form 1 mol of NH_3, then only half as much heat (46.19 kJ mol^{-1}) would be released. The thermochemical equations can be written as:

$$\mathrm{2N_2(g) + 6H_2(g) \rightarrow 4NH_3(g)}; \quad \Delta H^{\circ} = -184.8\ \mathrm{kJ\ mol^{-1}}$$
$$\tfrac{1}{2}\mathrm{N_2(g)} + \tfrac{3}{2}\mathrm{H_2(g) \rightarrow NH_3(g)}; \quad \Delta H^{\circ} = -46.19\ \mathrm{kJ\ mol^{-1}}$$

Because the coefficients of a thermochemical equation always mean *moles*, not molecules, we may use fractional coefficients.

2. When an equation is reversed – written in the opposite direction – the sign of ΔH° must also be reversed. For example, the thermochemical equation for the combustion of carbon in oxygen to give carbon dioxide is

$$\mathrm{C(s) + O_2(g) \rightarrow CO_2(g)}; \quad \Delta H^{\circ} = -393.5\ \mathrm{kJ\ mol^{-1}}$$

The reverse reaction would be the decomposition of carbon dioxide to carbon and oxygen. The law of conservation of energy requires that its value of ΔH° equals +393.5 kJ.

$$\mathrm{CO_2(g) \rightarrow C(s) + O_2(g)}; \quad \Delta H^{\circ} = +393.5\ \mathrm{kJ\ mol^{-1}}$$

In effect, these two thermochemical equations tell us that the combustion of carbon is exothermic (as indicated by the negative sign of ΔH°) and that the reverse reaction is endothermic and difficult to carry out. The same amount of energy is involved in both reactions; it is just the direction of energy flow that is different. We can reverse any thermochemical equation as long as we change the sign of its ΔH°.

3. Enthalpy changes depend only on the initial and final states, not on the path between them. This gives a method for combining known thermochemical equations in a way that will allow us to calculate an unknown ΔH° for some other reaction. Let us revisit the combustion of carbon to see how this works.

We can imagine two paths leading from 1 mole each of carbon and oxygen to 1 mol of carbon dioxide.

One-Step Path: Let C and O_2 react to give CO_2 directly.

$$\mathrm{C(s) + O_2(g) \rightarrow CO_2(g)}; \quad \Delta H^{\circ} = -393.5\ \mathrm{kJ\ mol^{-1}}$$

Two-Step Path: Let C and O_2 react to give CO, and then let CO react with more O_2 to give CO_2.

Step 1: $\mathrm{C(s)} + \tfrac{1}{2}\mathrm{O_2(g) \rightarrow CO(g)}; \quad \Delta H^{\circ} = -110.5\ \mathrm{kJ\ mol^{-1}}$

Step 2: $\mathrm{CO(g)}+\frac{1}{2}\mathrm{O_2(g)} \rightarrow \mathrm{CO_2(g)}; \quad \Delta H^\circ = -283.0\ \mathrm{kJ\,mol^{-1}}$

Overall, the two-step path consumes 1 mol each of C and O_2 to make 1 mol of CO_2, just like the one-step path. The initial and final states for the two routes to CO_2, in other words, are identical. Because ΔH° is a state function dependent only on the initial and final states and is independent of path, the values of ΔH° for both routes should be identical. We can see that this is exactly true simply by adding the equations for the two-step path and comparing the result with the equation for the single step.

Step 1: $\mathrm{C(s)}+\frac{1}{2}\mathrm{O_2(g)} \rightarrow \mathrm{CO(g)}; \quad \Delta H^\circ = -110.5\ \mathrm{kJ\,mol^{-1}}$

Step 2: $\mathrm{CO(g)}+\frac{1}{2}\mathrm{O_2(g)} \rightarrow \mathrm{CO_2(g)}; \quad \Delta H^\circ = -283.0\ \mathrm{kJ\,mol^{-1}}$

Overall reaction: $\mathrm{CO(g)}+\mathrm{C(s)}+\mathrm{O_2(g)} \rightarrow \mathrm{CO_2(g)}+\mathrm{CO(g)}; \quad \Delta H^\circ = -110.5+(-283.0) = -393.5\ \mathrm{kJ\,mol^{-1}}$

The equation resulting from adding Steps 1 and 2 has "CO(g)" appearing *identically* on opposite sides of the arrow. We can cancel them to obtain the overall equation.

Note: Such a cancellation is permitted only when both the formula and the physical state of a species are identical on opposite sides of the arrow.

The overall thermochemical equation for the two-step process, therefore, is

$$\mathrm{C(s)}+\mathrm{O_2(g)} \rightarrow \mathrm{CO_2(g)}; \quad \Delta H^\circ = -393.5\ \mathrm{kJ\,mol^{-1}}$$

The results, are thus identical for both routes to CO_2 both chemically and thermochemically.

7.12 | LAWS OF THERMOCHEMISTRY

Lavoisier–Laplace Law

It states that the enthalpy change accompanying a chemical process is same in magnitude but opposite in sign to the enthalpy change accompanying the same process in the reverse direction. This is also known as the **first law of thermochemistry**. For example, the formation of water from its constituent elements is an exothermic process with $\Delta H = -286$ kJ mol^{-1} whereas decomposition of water into its constituent elements is an endothermic process with $\Delta H = +286$ kJ mol^{-1}.

$$\mathrm{H_2(g)}+\tfrac{1}{2}\mathrm{O_2(g)} \rightarrow \mathrm{H_2O(l)} \quad \Delta H = -286\ \mathrm{kJ\ mol^{-1}}$$

$$\mathrm{H_2O(l)} \rightarrow \mathrm{H_2(g)}+\tfrac{1}{2}\mathrm{O_2(g)} \quad \Delta H = 286\ \mathrm{kJ\ mol^{-1}}$$

Hess's Law of Constant Heat Summation

Using the tools for manipulating equations, we should to be able to calculate ΔH° values simply by algebraic summing. G.H. Hess was the first to realize this so the associated law is called **Hess' law of heat summation** or simply **Hess' law**, which states that

The heat absorbed or liberated in a given chemical equation is always constant and is the same whether the process occurs in one step or in several steps.

Since ΔU and ΔH are state functions, the heat liberated or absorbed in a given reaction must also be independent of the way in which the reaction is brought about, that is, it depends only on the initial and final states of the system and not on the path followed to achieve that state. The value of ΔH° for any reaction that can be written in steps equals the sum of the values of ΔH° of each of the individual steps.

For example, we can verify Hess's law by considering the following thermochemical equations:

$$\tfrac{1}{2}\mathrm{N_2(g)}+\tfrac{1}{2}\mathrm{O_2(g)} \rightarrow \mathrm{NO(g)}; \quad \Delta H^\circ = +90.4\ \mathrm{kJ\,mol^{-1}}$$

$$\mathrm{NO(g)}+\tfrac{1}{2}\mathrm{O_2(g)} \rightarrow \mathrm{NO_2(g)}; \quad \Delta H^\circ = -56.6\ \mathrm{kJ\,mol^{-1}}$$

Suppose we add the two equations and then cancel anything that's the same on both sides.

$$\tfrac{1}{2}N_2(g)+\tfrac{1}{2}O_2(g)\rightarrow NO(g)$$
$$NO(g)+\tfrac{1}{2}O_2(g)\rightarrow NO_2(g)$$
$$\tfrac{1}{2}N_2(g)+NO(g)+\underbrace{\tfrac{1}{2}O_2(g)+\tfrac{1}{2}O_2(g)}_{O_2(g)}\rightarrow NO(g)+NO_2(g)$$

Notice that we have combined the two $\frac{1}{2}O_2$ to give $O_2(g)$. Rewriting the equation gives

$$\tfrac{1}{2}N_2(g)+O_2(g)\rightarrow NO_2(g)$$

According to Hess's law, we should be able to obtain ΔH° for this reaction by simply adding the ΔH° values for the equations we have added.

$$\Delta H^\circ = (+90.4)+(-56.6) = +33.8\ \text{kJ mol}^{-1}$$

In general, if the enthalpy of overall reaction reactants→ products is given by $\Delta_r H$ and the reaction can also take place in n number of steps, with reaction enthalpy $\Delta_r H_1, \Delta_r H_2, ..., \Delta_r H_n$, then

$$\Delta_r H = \Delta_r H_1 + \Delta_r H_2 + \cdots + \Delta_r H_n$$

The energy relationships among the alternative pathways for the same overall reaction are clearly seen using a graphical construction called an **enthalpy diagram**. Figure 7.19 is an enthalpy diagram for the formation of CO_2 from C and O_2. Each horizontal line corresponds to a certain total amount of enthalpy, which we cannot actually measure. We *can* measure differences in enthalpy, however, and that is what we use the diagram for. Lines higher up the enthalpy scale represent larger amounts of enthalpy, so going from a lower line to a higher line corresponds to an increase in enthalpy and a positive value for ΔH° (an endothermic change). The size of ΔH° is represented by the vertical distance between the two lines. Likewise, going from a higher line to a lower one represents a decrease in enthalpy and a negative value for ΔH° (an exothermic change).

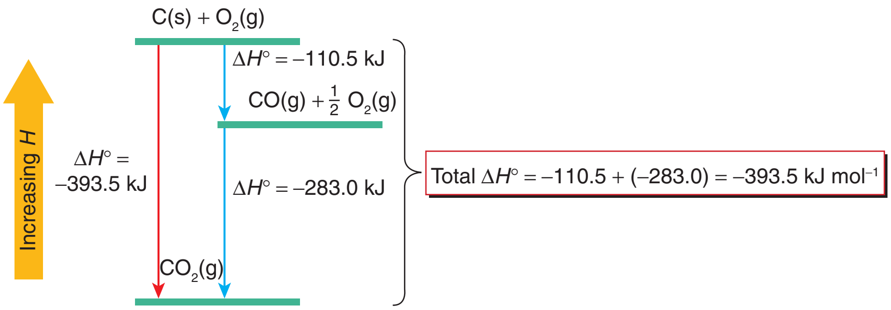


Figure 7.19 An enthalpy diagram for the formation of $CO_2(g)$ from its elements by two different paths.

Solved Example 7-29

Carbon monoxide is often used in metallurgy to remove oxygen from metal oxides and thereby give the free metal. The thermochemical equation for the reduction reaction of iron(III) oxide, Fe_2O_3, with CO is as follows:

$$Fe_2O_3(s)+3CO(g)\rightarrow 2Fe(s)+3CO_2(g);$$
$$\Delta H^\circ = -26.7\ \text{kJ mol}^{-1}$$

Using this equation and the equation for the combustion of CO,

$$CO(g)+\tfrac{1}{2}O_2(g)\rightarrow CO_2(g);\quad \Delta H^\circ = -283.0\ \text{kJ mol}^{-1}$$

Calculate the value of ΔH° for the following reaction

$$2Fe(s)+\tfrac{3}{2}O_2(g)\rightarrow Fe_2O_3(s)$$

Solution

We can manipulate the two given equations as follows.

Step 1: The target equation must have 2Fe on the *left*, but the first equation above has 2Fe to the *right* of the arrow. So we begin by getting the iron atoms to come on right. We achieve this by reversing the equation and reversing the sign of ΔH°, we have

$$2Fe(s)+3CO_2(g)\rightarrow Fe_2O_3(s)+3CO(g);$$
$$\Delta H^\circ = +26.7\ \text{kJ mol}^{-1}$$

Step 2: There must be $\frac{3}{2}O_2$ on the left, and we must be able to cancel *three* CO and *three* CO_2 when the equations are added. On multiplying the second of the equations given above by 3, we obtain the necessary coefficients. We also multiply the value of ΔH° of this equation with 3, because three times as many moles of substances are now involved in the reaction. When we have done this, we have

$$3CO(g) + \tfrac{3}{2}O_2(g) \rightarrow 3CO_2(g);$$
$$\Delta H^\circ = 3 \times (-283.0 \text{ kJ}) = -849.0 \text{ kJ mol}^{-1}$$

Adding both equations, we get

$$2Fe(s) + 3CO_2(g) \rightarrow Fe_2O_3(s) + 3CO(g); \Delta H^\circ = +26.7 \text{ kJ mol}^{-1}$$
$$3CO(g) + \tfrac{3}{2}O_2(g) \rightarrow 3CO_2(g);\ \Delta H^\circ = -849.0 \text{ kJ mol}^{-1}$$
$$2Fe(s) + \tfrac{3}{2}O_2(g) \rightarrow Fe_2O_3(s);\ \Delta H^\circ = -822.3 \text{ kJ mol}^{-1}$$

Thus, the value of ΔH° for the oxidation of 2 mol Fe(s) to 1 mol $Fe_2O_3(s)$ is –822.3 kJ mol^{-1}. (The reaction is *very* exothermic.)

Solved Example 7-30

For ethanol, C_2H_5OH, which is mixed with gasoline to make the fuel gasohol, ΔH_f = –277.63 kJ mol^{-1}. Calculate the number of kilojoules released by burning completely 3.78 L of ethanol. The density of ethanol is 0.787 g cm^{-3}. Use data in Table 7.3 for values.

Solution

The combustion reaction is $C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$. The enthalpy of the reaction is

$$\begin{aligned}\Delta H^\circ &= [3\Delta H_f^\circ(H_2O(l)) + 2\Delta H_f^\circ(CO_2(g))]\\ &\quad -[\Delta H_f^\circ(C_2H_5OH(l)) + 3\Delta H_f^\circ(O_2(g))]\\ &= 3(-285.9 \text{ kJ}) + 2(-393.5 \text{ kJ})\\ &\quad -(-277.63 \text{ kJ}) = -1367.1 \text{ kJ mol}^{-1}\end{aligned}$$

The heat released in burning completely 3.78 L of ethanol is

$$3.785 \text{ L}\left(\frac{1000 \text{ mL}}{1 \text{ L}}\right)\left(\frac{0.787 \text{ g}}{1 \text{ mL}}\right)\left(\frac{1 \text{ mol}}{46.07 \text{ g}}\right)\left(\frac{-1367 \text{ kJ}}{1 \text{ mol}}\right)$$
$$= -88400 \text{ kJ}$$

Solved Example 7-31

Given the following thermochemical equations:

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g);\ \Delta H^\circ = -113.2 \text{ kJ mol}^{-1}$$
$$2N_2O(g) + 3O_2(g) \rightarrow 4NO_2(g);\ \Delta H^\circ = -28.0 \text{ kJ mol}^{-1}$$

calculate ΔH° for this reaction: $N_2O(g) + \frac{1}{2}O_2(g) \rightarrow 2NO(g)$

Solution

First, we divide the second reaction by 2:

$$N_2O(g) + \tfrac{3}{2}O_2(g) \rightarrow 2NO_2(g) \qquad \Delta H = -14.0 \text{ kJ mol}^{-1}$$

Now, reversing the first reaction, we get

$$2NO_2(g) \rightarrow 2NO(g) + O_2(g) \qquad \Delta H = 113.2 \text{ kJ mol}^{-1}$$

Adding the above reactions, we get

$$N_2O(g) + \tfrac{3}{2}O_2(g) \rightarrow 2NO_2(g) \qquad \Delta H^\circ = -14.0 \text{ kJ mol}^{-1}$$
$$2NO_2(g) \rightarrow 2NO(g) + O_2(g) \qquad \Delta H^\circ = 113.2 \text{ kJ mol}^{-1}$$
$$N_2O(g) + \tfrac{1}{2}O_2(g) \rightarrow 2NO(g) \qquad \Delta H^\circ = +99.2 \text{ kJ mol}^{-1}$$

7.13 | ENTHALPIES OF DIFFERENT TYPES OF REACTIONS

Enthalpy data for various types of reactions have been collated and is used for determining heat of reaction of any related reaction using Hess's law. It is useful to classify reactions and associated enthalpies into different types, such as formation, neutralization, combustion, atomization and phase change reactions.

Enthalpy of Neutralization

It is the enthalpy change of a system when 1 g-equiv. of an acid is neutralized by 1 g-equiv. of a base (or vice versa) in a dilute solution. For example, in the following neutralization reaction ΔH = –57.54 kJ mol^{-1}.

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O$$

Enthalpy of neutralization of a strong acid and strong base is – 57.54 kJ mol^{-1}, no matter which acid or base is employed. This is because it amounts to formation of water from its ions, and this value remains constant irrespective of the source of the ions.

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l) \quad \Delta H = -57.54 \text{ kJ mol}^{-1}$$

However, in case of neutralization reactions where either the acid or base is weak or both are weak, the apparent value of heat of neutralization is less than 57.54 kJ mol^{-1} (or 13.7 kcal). For example, consider the following reactions:

$$\underset{\text{Weak}}{CH_3COOH(aq)} + \underset{\text{Strong}}{NaOH(aq)} \rightarrow CH_3COONa(aq) + H_2O; \Delta H = -56.1 \text{ kJ}$$

$$\underset{\text{Strong}}{HCl(aq)} + \underset{\text{Weak}}{NH_4OH(aq)} \rightarrow NH_4Cl(aq) + H_2O; \Delta H = -51.5 \text{ kJ}$$

$$\underset{\text{Weak}}{CH_3COOH(aq)} + \underset{\text{Weak}}{NH_4OH(aq)} \rightarrow CH_3COONH_4(aq) + H_2O; \Delta H = -49.8 \text{ kJ}$$

This can be explained on the basis that a part of heat released during neutralization is used for bringing about the dissociation of the weak acid or base, which is not completely dissociated in the reaction medium.

Let us consider neutralization reaction between monobasic acids and monoacidic bases, such that SA = strong acid, SB = strong base, WA = weak acid and WB = weak base. Then enthalpy of neutralization between these can be summarized as:

Case 1:

$$\underset{(1\text{ mol})}{SA} + \underset{(1\text{ mol})}{SB} \rightarrow \text{Salt} + H_2O$$

$$\Delta H_{\text{neutralization}} = -57.2 \text{ kJ/mol}$$

$$WA + SB \rightarrow \text{Salt} + H_2O$$

Case 2:

$$SA + WB \rightarrow \text{Salt} + H_2O$$

$$WA + WB \rightarrow \text{Salt} + H_2O$$

$$\Delta H_{\text{neutralization}} = -57.2 \text{ kJ/mol} + q$$

where q is the heat required to ionize the weak components completely. Note that positive sign indicates that heat is required.

Standard Enthalpy of Combustion (Symbol: $\Delta_c H°$)

It is the enthalpy change when one mole of the substance is completely burnt in excess of air. The **standard heat of combustion, $\Delta_c H°$**, of a substance is the amount of heat released when 1 mol of a fuel substance is completely burned in pure oxygen gas, with all reactants and products brought to 25°C and 1 bar of pressure. For example, the enthalpy change involved in burning of carbon in presence of excess oxygen is given by $\Delta H = -395.65$ kJ mol^{-1}. All carbon in the fuel becomes carbon dioxide gas, and all the fuel's hydrogen becomes liquid water. *Combustion reactions are always exothermic*, so $\Delta_c H°$ is always negative.

The combustion of fuels such as petrol, cooking gas, kerosene, etc., produces heat that is used for cooking and running automobiles and machinery. The food consumed by living things also undergoes combustion in the body and yields energy for doing work. For example, athletes consume glucose for gaining instant energy because of its high heat of combustion.

Enthalpy of Atomization (Symbol: $\Delta_a H°$)

It is the amount of energy needed to break all the chemical bonds in 1 mol of molecules to give gaseous atoms as products. For example, the atomization of methane is

$$CH_4(g) \rightarrow C(g) + 4H(g); \quad \Delta_a H° = 1665 \text{ kJ mol}^{-1}$$

and the enthalpy change for the process is $\Delta_a H°$. For this particular molecule, ΔH corresponds to the total amount of energy needed to break all the C–H bonds in 1 mol of CH_4; therefore, division of $\Delta_a H°$ by 4 would give the average C–H bond enthalpy in methane, expressed in kJ mol^{-1}. For diatomic molecules such as dihydrogen, chlorine, oxygen, etc., the enthalpy of atomization is same as the bond dissociation enthalpy.

$$Cl_2(g) \rightarrow 2Cl(g); \quad \Delta_a H° = 242.0 \text{ kJ mol}^{-1}$$

For substances in atomic state, the enthalpy of atomization corresponds to the enthalpy for phase change to gaseous state. For example, in the reaction

$$\mathrm{Na(s)} \rightarrow \mathrm{Na(g)}; \quad \Delta_a H^\circ = 108.4.0\ \mathrm{kJ\ mol^{-1}}$$

The enthalpy of atomization is the same as the enthalpy of sublimation (fusion + vaporization).

Enthalpy of Solution (Symbol: $\Delta_{sol}H°$)

The formation of a solution is associated with energy exchanges because intermolecular attractive forces are important when liquids and solids are involved. The total energy absorbed or released when a solute dissolves in a solvent at constant pressure to make a solution is called the **molar enthalpy of solution**, or usually just the **heat of solution, $\Delta_{sol}H$**.

Energy is required to separate the particles of solute and also those of the solvent and make them spread out to make room for each other. This step is *endothermic*, because we must overcome the attractions between molecules to spread the particles out. However, once the particles come back together as a *solution*, the attractive forces between approaching solute and solvent particles yield a decrease in the system's potential energy, and this is an *exothermic* change. The enthalpy of solution, $\Delta_{sol}H$, is simply the net result of these two opposing enthalpy contributions.

The heat of solution for a solid is the lattice enthalpy plus the solvation enthalpy. Let us see how by taking example of dissolution of an ionic/covalent solute in a solvent. For a solid dissolving in a liquid, it is convenient to imagine a two-step path.

Step 1: *Vaporize the solid to form individual solute particles.* The particles are molecules for molecular substances and ions for ionic compounds. The energy absorbed is the lattice enthalpy of the solid.

Step 2: *Bring the separated gaseous solute particles into the solvent to form the solution.* This step is exothermic, and the enthalpy change when the particles from one mole of solute are dissolved in the solvent is called the **solvation enthalpy**. If the solvent is water, the solvation enthalpy can also be called the **hydration enthalpy**.

The enthalpy diagram showing these steps for potassium iodide is given in Fig. 7.20. Step 1 corresponds to the lattice enthalpy of KI, which is represented by the thermochemical equation

$$\mathrm{KI(s)} \rightarrow \mathrm{K^+(g)} + \mathrm{I^-(g)}; \quad \Delta H^\circ = +632\ \mathrm{kJ\ mol^{-1}}$$

Step 2 corresponds to the hydration enthalpy of gaseous K^+ and I^- ions.

$$\mathrm{K^+(g)} + \mathrm{I^-(g)} \rightarrow \mathrm{K^+(aq)} + \mathrm{I^-(aq)}; \ \Delta H^\circ = -619\ \mathrm{kJ\ mol^{-1}}$$

Lattice enthalpy: $\mathrm{KI(s)} \rightarrow \mathrm{K^+(g)} + \mathrm{I^-(g)}$;

$\Delta H^\circ = +632\ \mathrm{kJ\ mol^{-1}}$

Hydration enthalpy: $\mathrm{K^+(g)} + \mathrm{I^-(g)} \rightarrow \mathrm{K^+(aq)} + \mathrm{I^-(aq)}$;

$\Delta H^\circ = -619\ \mathrm{kJ\ mol^{-1}}$

Total: $\mathrm{KI(s)} \rightarrow \mathrm{K^+(aq)} + \mathrm{I^-(aq)}$; $\Delta_{sol}H^\circ = +13\ \mathrm{kJ\ mol^{-1}}$

Thus, the standard heat of solution is given by

$$\Delta_{sol}H^\circ = \Delta_{lattice}H^\circ + \Delta_{hydration}H^\circ$$

The *enthalpy of solution* is obtained from the sum of the equations for Steps 1 and 2 and is the enthalpy change when one mole of crystalline KI dissolves in water (corresponding to the direct path in Fig. 7.20).

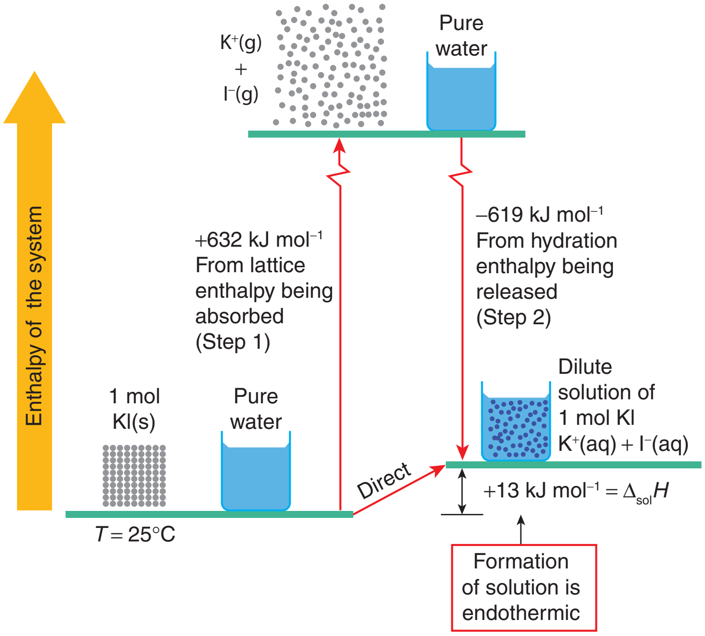


Figure 7.20 Enthalpy diagram for the heat of solution of one mole of potassium iodide.

$$\mathrm{KI(s)} \rightarrow \mathrm{K^+(aq)} + \mathrm{I^-(aq)}; \quad \Delta_{sol}H^\circ = +13\ \mathrm{kJ\ mol^{-1}}$$

The value of $\Delta_{sol}H^\circ$ indicates that the solution process is endothermic for KI, in agreement with the observation that when KI is added to water and the mixture is stirred, it becomes cool as the KI dissolves. The solubility of most salts increases in water with increase in temperature. If the lattice enthalpy of the salt is high, the solubility of the substance in the solvent is low.

Solved Example 7-32

n-Octane, $C_8H_{18}(l)$, has a standard heat of combustion of 5450.5 kJ mol^{-1}. A 15 L automobile fuel tank could hold about 480 mol of *n*-octane. How much heat could be produced by burning a full tank of *n*-octane?

Solution

$$\text{Heat produced} = (480)\left(\frac{5450.5}{1}\right) = 2.62 \times 10^6 \text{ kJ}$$

Solved Example 7-33

Diborane is a potential rocket fuel which undergoes combustion according to the reaction,

$$B_2H_6(g) + 3O_2(g) \rightarrow B_2O_3(s) + 3H_2O(g)$$

From the following data, calculate the enthalpy change for the combustion of diborane: **(IIT-JEE 2000)**

$$2B(s) + \tfrac{3}{2}O_2(g) \rightarrow B_2O_2(s);\ \Delta H = -1273\ \text{kJ mol}^{-1}$$

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(1);\ \Delta H = -286\ \text{kJ mol}^{-1}$$

$$H_2O(l) \rightarrow H_2O(g);\ \Delta H = 44\ \text{kJ mol}^{-1}$$

$$2B(s) + 3H_2(g) \rightarrow B_2H_6(g);\ \Delta H = 36\ \text{kJ mol}^{-1}$$

Solution

From the given data, the heat of combustion reaction of diborane can be calculated as

$$B_2H_6(g) + 3O_2(g) \rightarrow B_2O_3(s) + 3H_2O(g)$$

$$\begin{aligned}\Delta_r H^\circ &= \Delta H_f^\circ(B_2O_3) + 3\times[\Delta H_f^\circ(H_2O)\\ &\quad + \Delta_{vap}H^\circ(H_2O)] - \Delta H_f^\circ(B_2H_6)\end{aligned}$$

$$\text{Now, } \Delta_{vap}H^\circ(H_2O) = \Delta H_f^\circ(H_2O) + 44 = -242\ \text{kJ mol}^{-1}$$

$$\begin{aligned}\Delta_c H^\circ(B_2H_6) &= -1273 + 3(-242) - 36\\ \text{Therefore,}\quad &= -2035\ \text{kJ mol}^{-1}\end{aligned}$$

Solved Example 7-34

The heat of combustion, $\Delta_c H^\circ$ of acetone, CH_3COCH_3, is 1790.4 kJ mol^{-1}. How many kilojoules of heat are evolved in the combustion of 12.5 g of acetone? (M. wt. of acetone = 58.077 g/mol)

Solution

$$\text{Heat evolved} = (12.5\ \text{g}\ C_3H_6O)$$

$$\left(\frac{1\ \text{mol}\ CH_3COCH_3}{58.077\ \text{g}\ CH_3COCH_3}\right)\left(\frac{1790.4\ \text{kJ}}{1\ \text{mol}\ CH_3COCH_3}\right) = 385\ \text{kJ mol}^{-1}$$

Solved Example 7-35

The enthalpy change for the combustion of one mole of a compound under standard conditions is called the standard heat of combustion, and its symbol is $\Delta_c H^\circ$. The value for sucrose, $C_{12}H_{22}O_{11}$ is -5.65×10^3 kJ mol^{-1}. Write the thermochemical equation for the combustion of 1 mol of sucrose and calculate the value of ΔH_f° for this compound. The sole products of combustion are $CO_2(g)$ and $H_2O(l)$. Use data in Table 7.3 as necessary.

Solution

The enthalpy of combustion is given by $\Delta_c H^\circ = \Sigma\Delta_f H^\circ(\text{products}) - \Sigma\Delta_f H^\circ(\text{reactants})$. Substituting values, we get

$$\begin{aligned}\Delta_c H^\circ &= [12\ \text{mol}\ CO_2 \times \Delta_f H^\circ(CO_2(g)) + 11\ \text{mol}\ H_2O\\ &\quad \times \Delta_f H^\circ(H_2O(l))]\\ &\quad - [1\ \text{mol}\ C_{12}H_{22}O_{11} \times \Delta_f H^\circ(C_{12}H_{22}O_{11}(s))\\ &\quad + 12\ \text{mol}\ O_2 \times \Delta_f H^\circ(O_2(g))]\end{aligned}$$

Rearranging and realizing that $\Delta_f H^\circ(O_2(g)) = 0$, we get

$$\begin{aligned}\Delta_f H^\circ(C_{12}H_{22}O_{11}(s)) &= 12\Delta_f H^\circ(CO_2(g))\\ &\quad + 11\Delta_f H^\circ(H_2O(l)) - \Delta_c H^\circ\end{aligned}$$

or

$$\begin{aligned}\Delta_f H^\circ(C_{12}H_{22}{>}_{11}(s)) &= 12(-393) + 11(-285.9) < (-5.65\times 10^3)\\ &= -2.21 \times 10^3\ \text{kJ mol}^{-1}\end{aligned}$$

7.14 | BOND ENTHALPY AND BOND DISSOCIATION ENTHALPY

Bond enthalpy (**$\Delta_{\text{bond}}H^\circ$**) is the amount of energy required to break all the bonds present in one mole of a compound. Likewise, the energy liberated when a bond is formed between two atoms to form one mole of a compound is also called bond enthalpy. It is also referred to as enthalpy of formation of bond. In simpler words, bond enthalpy measures the strength of the bond, that is, the force with which the atoms are bonded together. The enthalpy changes associated with making or breaking of chemical bonds are thus expressed in terms of:

1. Bond dissociation enthalpy
2. Mean bond enthalpy

Bond enthalpy depends on many factors, such as electronegativity of the atoms, size of the atoms, bond length, etc. The chemical environment of the bond influences the bond enthalpy. Bond breaking is an endothermic process, and is thus accompanied by absorption of energy. This leads to a positive value of bond dissociation enthalpy. On the other hand, bond formation is an exothermic process, and is thus accompanied by a release of energy. This leads to a negative value of bond enthalpy.

The bond enthalpies can be discussed in terms of diatomic and polyatomic molecules.

1. **Diatomic molecules:** For all diatomic molecules, the bond dissociation enthalpy is same as the enthalpy of atomization. By definition, bond dissociation enthalpy is the change in enthalpy when one mole of gaseous covalent compound is broken into constituent atoms in the gas phase. For example, when one mole of oxygen molecules in gaseous state dissociates to form oxygen atoms, the bond dissociation enthalpy is the same as the enthalpy of atomization of oxygen.

$$O_2(g) \rightarrow 2O(g); \quad \Delta_{O—O}H^\circ = 428 \text{ kJ mol}^{-1}$$

Similarly, this is also true for other diatomic molecules such as H_2, Cl_2, etc.

$$H_2(g) \rightarrow 2H(g); \quad \Delta_{H—H}H^\circ = 435 \text{ kJ mol}^{-1}$$
$$Cl_2(g) \rightarrow 2Cl(g); \quad \Delta_{Cl—Cl}H^\circ = 242 \text{ kJ mol}^{-1}$$

The bond enthalpies of simple diatomic molecules are measured spectroscopically.

2. **Polyatomic molecules:** For complex polyatomic molecules, the bond dissociation enthalpy for different bonds is different within the same molecule. For example, let us consider a polyatomic molecule like ammonia, NH_3. The enthalpy of atomization is

$$NH_3(g) \rightarrow N(g) + 3H(g); \quad \Delta_a H^\circ = 1175.7 \text{ kJ mol}^{-1}$$

The sequential dissociation of N—H bonds, which are identical in bond length and energy, have different enthalpies for dissociation.

$$NH_3(g) \rightarrow NH_2(g) + H(g); \quad \Delta_{\text{bond}}H^\circ = 449 \text{ kJ mol}^{-1}$$
$$NH_2(g) \rightarrow NH(g) + H(g); \quad \Delta_{\text{bond}}H^\circ = 384 \text{ kJ mol}^{-1}$$
$$NH(g) \rightarrow N(g) + H(g); \quad \Delta_{\text{bond}}H^\circ = 339 \text{ kJ mol}^{-1}$$

The variation in breaking of individual N—H bonds is large, therefore, we consider the mean bond enthalpy of N

Table 7.4 Some average bond enthalpies

Bond	Bond enthalpy (kJ mol^{-1})	Bond	Bond enthalpy (kJ mol^{-1})
C C	348	C Br	276
C C	612	C I	238
C C	960	H H	436
C H	412	H F	565
C N	305	H Cl	431
C N	613	H Br	366
C≡N	890	H I	299
C O	360	H N	388
C O	743	H O	463
C F	484	H S	338
C Cl	338	H Si	376

The bond enthalpies can be used for predicting the enthalpies of reactions taking place in gaseous phase and for estimating the heats of formation of compounds.

1. **Determination of enthalpy of reaction:** Bond enthalpy is useful for calculating enthalpies of reaction for gaseous reactions which involve substances having covalent bonds. For example, consider the formation of ethane from ethylene.

H_2C

3. **Determination of resonance energy:** For a compound exhibiting resonance, there is a considerable difference between the enthalpy of formation or dissociation as calculated from bond energies and that determined experimentally. This difference arises due to stabilization by resonance and is a measure of the resonance energy. For example, consider the dissociation of benzene

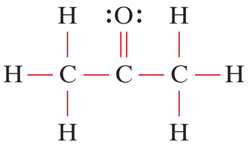
$$C_6H_6(g) \rightarrow 6C(g) + 6H(g)$$

The calculated bond dissociation enthalpy

$$\Delta H_d = 3(\Delta H_C$$

Solved Example 7-38

Acetone, the solvent usually found in nail polish remover and has the structural formula



Approximately how much energy would be released during the formation of the bonds in one mole of acetone molecules?

Solution

The energy released during the formation of 1 mol of acetone is equal to the sum of all of the bond energies in the molecule:

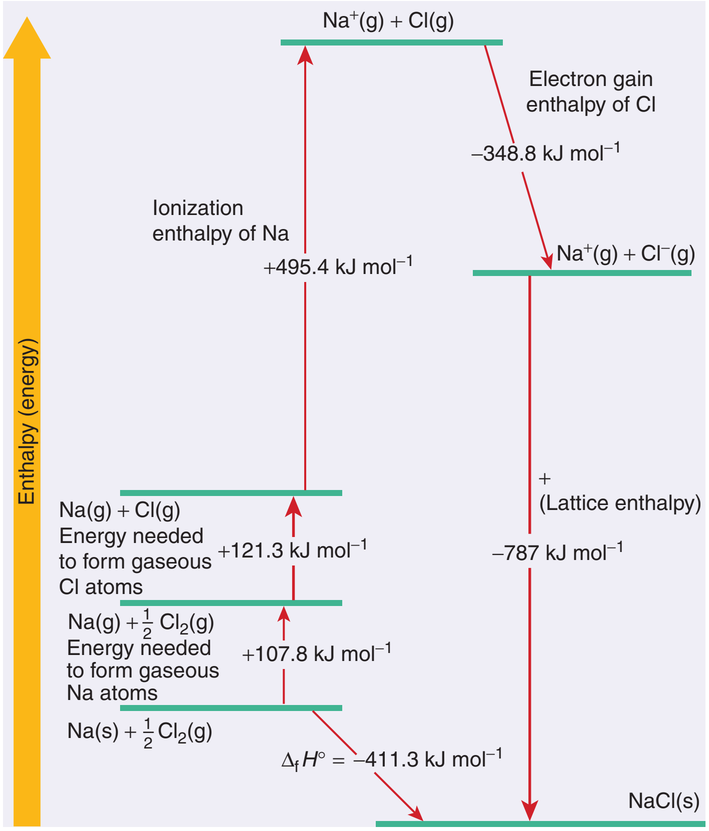
For the six C

Solved Example 7-40

The standard heat of formation of ethanol vapor, $C_2H_5OH(g)$, is –235.3 kJ mol^{-1}. Use the data in Table 7.4 and the average bond energies for C only energy terms involved in the formation of NaCl, the heat of formation would be endothermic and the compound would be unstable; it could not be formed by direct combination of the elements.

The last step on the right finally brings us to solid NaCl and corresponds to the negative of the lattice enthalpy. (Remember, the lattice enthalpy is defined as the energy needed to *separate* the ions; in the last step, we are *bringing the ions together* to form the solid.) To make the net energy changes the same along both paths, the energy released when the ions condense to form the solid must equal –787.0 kJ. Therefore, the calculated lattice enthalpy of NaCl must be +787.0 kJ mol^{-1}.

The path at the lower left labelled $\Delta_f H^o$ leads directly to NaCl(s). The upper path involves the formation of gaseous atoms from the elements, then the formation of gaseous ions from the atoms, and finally the condensation of Na^+ and Cl^- ions to give solid NaCl. The final step releases energy equivalent to the lattice enthalpy. The enthalpy changes accompanying each step can be listed as:



Enthalpy (energy)
$Na^+(g) + Cl(g)$
Electron gain enthalpy of Cl
–348.8 kJ mol^{-1}
Ionization enthalpy of Na
+495.4 kJ mol^{-1}
$Na^+(g) + Cl^-(g)$
+ (Lattice enthalpy)
–787 kJ mol^{-1}
Na(g) + Cl(g)
Energy needed to form gaseous Cl atoms
+121.3 kJ mol^{-1}
$Na(g) + \frac{1}{2}Cl_2(g)$
Energy needed to form gaseous Na atoms
+107.8 kJ mol^{-1}
$Na(s) + \frac{1}{2}Cl_2(g)$
$\Delta_f H^o$ = –411.3 kJ mol^{-1}
NaCl(s)

Figure 7.22 Born–Haber cycle for sodium chloride.

1. Sublimation of sodium metal:
   $Na(s) \rightarrow Na(g); \quad \Delta_{sub}H^o = 107.8 \text{ kJ mol}^{-1}$
2. Ionization of sodium atoms:
   $Na(g) \rightarrow Na^+(g) + e^-; \quad \Delta_{ion}H^o = 495.4 \text{ kJ mol}^{-1}$
3. Dissociation of chlorine into atoms:
   $\frac{1}{2}Cl_2(g) \rightarrow Cl(g); \quad \frac{1}{2}\Delta_{bond}H^o = 121.3 \text{ kJ mol}^{-1}$
4. Gain of electron by chlorine: $Cl(g) + e^- \rightarrow Cl^-(g); \quad \Delta_{\text{electron gain}}H^o = -348.8 \text{ kJ mol}^{-1}$
5. The lattice enthalpy: $Na^+(g) + Cl^-(g) \rightarrow Na^+Cl^-(s);$

$$\Delta_{\text{lattice}}H^o = 411.3 + 107.8 + 121.3 + 495.4 - 348.8 \text{ kJ mol}^{-1} = 787.0 \text{ kJ mol}^{-1}$$

The lattice enthalpy also becomes larger as the amount of charge on the ions increases, because more highly charged ions attract each other more strongly. Thus, salts of Ca^{2+} have larger lattice enthalpies than comparable salts of Na^+, and those containing Al^{3+} have even larger lattice energies.

Besides affecting the ability of ionic compounds to form, lattice energies are also important in determining the solubilities of ionic compounds in water and other solvents.

Solved Example 7-41

Find the electron affinity of chlorine from the following data (in kcal mol^{-1}). The enthalpy of formation of LiCl is –97.5; lattice energy of LiCl = 197.7; dissociation energy of chlorine = 57.6; enthalpy of sublimation of Li = 38.3; ionization energy of Li = 123.8.

Solution

For the ionic compound LiCl, we have

$$\Delta_{\text{lattice}}H^o_{\text{LiCl}} = \Delta_{EA}H^o_{Cl} - \Delta_f H^o_{\text{LiCl}} + \frac{1}{2}\Delta_{BE}H^o_{Cl_2} + \Delta_{sub}H^o_{Li} + \Delta_{IE}H^o_{Li}$$

Substituting values, we get

$$197.7 = \Delta_{EA}H^o_{Cl} - (-97.5) + \frac{1}{2}(57.6) + (38.3) + (123.8)$$

Solving, we get $\Delta_{EA}H^o_{Cl} = -90.7 \text{ kcal mol}^{-1}$.

Solved Example 7-42

(a) Write all energy changes involve in Born–Haber cycle for the formation of calcium oxide.

(b) Calculate the lattice enthalpy of calcium oxide from the following data (kJ mol^{-1}): $\Delta_a H^o$ of Ca(s) = 178; $\Delta_{IE1}H^o$ of Ca(g) = 590; $\Delta_{IE2}H^o$ of Ca(g) = 1150; $\Delta_a H^o$ of O_2(g) = 249; $\Delta_{EA1}H^o$ of O(g) = –141; $\Delta_{EA2}H^o$ of O(g) = 844; ΔH_f^o of CaO(s) = –635.

Solution

(a) The energy changes are as follows:

Enthalpy of atomization of Ca(s): $Ca(s) \rightarrow Ca(g); \Delta_a H^o$

First ionization energy of Ca(g): $Ca(g) \rightarrow Ca^+(g) + e^-; \Delta_{IE1}H^o$

Second ionization energy of Ca(g): $Ca^+(g) \rightarrow Ca^{2+}(g) + e^-; \Delta_{IE2}H^o$

Enthalpy of atomization of O_2(g): $\frac{1}{2}O_2(g) \rightarrow 2O(g); \Delta_a H^o$

First electron affinity of O(g): $O(g) + e^- \rightarrow O(g); \Delta_{EA1}H^o$

Second electron affinity of O(g): $O^-(g) + e^- \rightarrow O^{2-}(g); \Delta_{EA2}H^o$

Enthalpy of formation of CaO(s): $Ca(s) + \frac{1}{2}O_2(g) \rightarrow CaO(s); \Delta_f H^o$

Lattice enthalpy of CaO(s): $Ca^{2+}(g) + O^{2-}(g) \rightarrow CaO(s); \Delta_{lattice}H^o$

(b) From Hess's law, we have

$$\Delta_{lattice}H^o + \Delta_f H^o = \Delta_a H^o(Ca) + \Delta_{IE1}H^o + \Delta_{IE2}H^o + \Delta_a H^o(O_2) + \Delta_{EA1}H^o + \Delta_{EA2}H^o$$

Substituting values, we get,

$$\Delta_{lattice}H^o = 178 + 590 + 1150 + 249 + (-141) + 844 - (-635)$$

Solving, we get $\Delta_{lattice}H^o = 3505$ kJ mol^{-1}.

7.15 | SPONTANEITY

The first law specifies that the energy of an isolated system is constant and that one form of energy can be converted into another. However, it does not indicate or predict the feasibility and extent of such an energy conversion. It establishes the relation between internal energy and enthalpy and provides expressions for heat changes occurring at constant volume or pressure. However, it does not specify the direction of heat change or flow.

We know from experience that heat flow is unidirectional and it flows from an object at higher temperature to an object at lower temperature. A large number of processes in nature proceed preferentially in one direction, for example, diffusion of gas from higher to lower pressure, neutralization of acid by base, a gas expanding to fill up the balloon, etc. Such processes which occur on their own accord are called **spontaneous processes**. These do not necessarily take place instantaneously, but are favorable and feasible.

The rate at which the spontaneous processes occur, range from very slow to very fast. For example, the exposure of photographic film are rapid spontaneous processes, hydrogen and oxygen gases can be mixed and left at room temperature without any significant formation of water. Thus, we can say that a spontaneous process has potential to occur without the aid of an external agency but need not take place instantaneously and at a fast rate. On the other hand, the decomposition of water into hydrogen and oxygen gas is a non-spontaneous process, but it can take place when an electric current is passed through it. The process of electrolysis continues till the current is maintained, thus illustrating that the non-spontaneous process will continue only till it receives outside assistance.

Enthalpy a Criterion for Spontaneity

We need to understand the driving force for the spontaneous change and the factors that will determine in which direction it will proceed. In physical process such as flow of water from hill top to the ground level or flow of heat from high to low temperatures can be understood in terms of the tendency of the system towards low energy state. By analogy, we can presume that chemical reactions proceed spontaneously in direction of lower energy. Spontaneous processes have a tendency to proceed in the direction of lower enthalpy. As a result, majority of exothermic chemical changes are spontaneous. For example,

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g); \qquad \Delta H^\circ = -92.38 \text{ kJ mol}^{-1}$$

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g); \quad \Delta H^\circ = -802.3 \text{ kJ mol}^{-1}$$

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(l); \qquad \Delta H^\circ = -285.9 \text{ kJ mol}^{-1}$$

However, if enthalpy were the only criteria for spontaneity, we would not expect endothermic processes to be spontaneous. However, there are a number of endothermic processes which are also spontaneous. For example,

$$\tfrac{1}{2}N_2(g) + O_2(g) \rightarrow NO_2(g); \quad \Delta H^\circ = +33.8 \text{ kJ mol}^{-1}$$

$$\tfrac{1}{2}N_2(g) + \tfrac{1}{2}O_2(g) \rightarrow NO(g); \quad \Delta H^\circ = +90.4 \text{ kJ mol}^{-1}$$

The enthalpy diagram in Fig. 7.23 shows that the exothermic processes proceed with lowering of energy, whereas endothermic processes proceed with increase in energy.

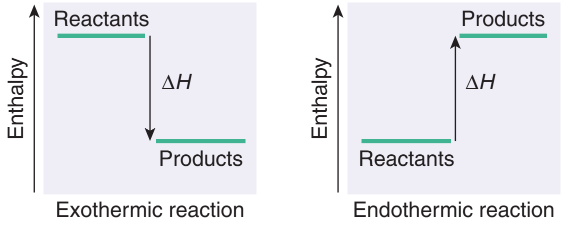


Figure 7.23 Enthalpy diagram for exothermic and endothermic processes.

7.16 | CARNOT CYCLE

Carnot cycle is the ideal cycle of operation of a heat engine, devised by Sadi Carnot. It is used to calculate the maximum extent to which heat can be converted to work. The direction of a particular spontaneous transformation can be ascertained with the help of the second law of thermodynamics.

Carnot cycle was assumed to be a different reversible system operating between two temperatures. In one complete cycle, it involves two isothermal and two adiabatic processes (Fig. 7.24). The working substance is an ideal gas.

Let us consider one gram mole of an ideal gas enclosed in the cylinder. Let p_1, V_1, T_1 be the initial pressure, volume, and temperature of the gas. Figure 7.24 shows the basic process of Carnot cycle which consists of four processes namely (a) isothermal expansion, (b) adiabatic expansion, (c) isothermal compression and (d) adiabatic compression.

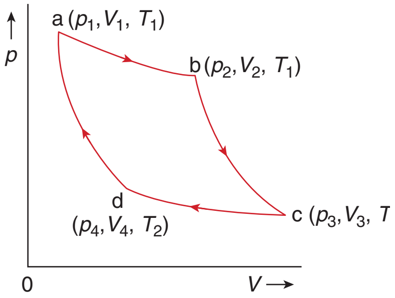


Figure 7.24 *p–V* diagram for Carnot engine.

Step 1 Isothermal expansion: The isothermal expansion of the gas takes place between point **a** and **b** of Fig. 7.24 taking its state from (p_1, V_1, T_1) to (p_2, V_2, T_1). Heat (q_1) is absorbed by the gas from the reservoir at temperature T_1. If the gas expands from V_1 to V_2 isothermally, the work done w_1 by the gas is given by

$$w_1 = nRT_1 \ln\left(\frac{V_2}{V_1}\right) \tag{7.25}$$

Step 2 Adiabatic expansion: The adiabatic expansion of the gas takes place between points **b** and **c**, taking its state from (p_2, V_2, T_1) to (p_3, V_3, T_2). When the gas expands from V_2 to V_3 adiabatically, the work done w_2 by the gas is given by

$$w_2 = nR\left(\frac{T_1 - T_2}{\gamma - 1}\right) \tag{7.26}$$

Step 3 Isothermal compression: The isothermal compression of the gas takes place between points **c** and **d** taking its state from (p_3, V_3, T_2) to (p_4, V_4, T_2).

When the gas compresses from V_3 to V_4 isothermally, the work done w_3 by the gas is given by

$$w_3 = nRT_2 \ln\left(\frac{V_3}{V_2}\right) \tag{7.27}$$

Heat (q_2) is released by the gas to the reservoir at temperature T_2.

Step 4 Adiabatic compression: The adiabatic compression of the gas takes place between points **d** and **a** taking its state from (p_4, V_4, T_2) to (p_1, V_1, T_1). When the gas is compressed from V_4 to V_1 adiabatically, the work done w_4 by the gas is given by

$$w_4 = nR\left(\frac{T_1 - T_2}{\gamma - 1}\right)$$

Now, the total work done during the complete one cycle is given by

$$w = w_1 + w_2 - w_3 - w_4$$

$$w = nRT_1 \ln\left(\frac{V_2}{V_1}\right) - nRT_2 \ln\left(\frac{V_3}{V_4}\right)$$

Now, Step 2 is an adiabatic process, therefore,

$$T_1 V_2^{\gamma-1} = T_2 V_3^{\gamma-1}$$

that is,

$$\frac{V_2}{V_3} = \left(\frac{T_2}{T_1}\right)^{1/(\gamma-1)} \tag{7.28}$$

Similarly, since Step 4 is an adiabatic process, therefore,

$$T_2 V_4^{\gamma-1} = T_1 V_1^{\gamma-1}$$

that is,

$$\frac{V_1}{V_4} = \left(\frac{T_2}{T_1}\right)^{1/(\gamma-1)} \tag{7.29}$$

From Eqs. (7.28) and (7.29), we have

$$\frac{V_3}{V_4} = \frac{V_2}{V_1} \tag{7.30}$$

Now, the efficiency of the Carnot's engine is given by

$$\eta = \frac{w}{q_1} = 1 - \frac{q_2}{q_1} = 1 - \left(\frac{T_2}{T_1}\right)\frac{\ln(V_3/V_4)}{\ln(V_2/V_1)}$$

or,

$$\eta = 1 - \frac{T_2}{T_1} \qquad \text{using Eq. (7.30)}$$

We have

$$1 - \frac{q_2}{q_1} = 1 - \frac{T_2}{T_1}$$

Therefore,

$$\frac{q_2}{q_1} = \frac{T_2}{T_1} \Rightarrow \frac{q_1}{T_1} - \frac{q_2}{T_2} = 0$$

$$\frac{q_1}{T_1} + 0 + \frac{(-q_2)}{T_2} + 0 = 0$$

$$\oint \frac{dq_{\text{rev}}}{T} = 0 \qquad (\because \text{reversible process})$$

Thus $\frac{dq_{\text{rev}}}{T}$ is a state function.

We define $\int \frac{dq_{\text{rev}}}{T} = \Delta S$

where S is the entropy and ΔS is the entropy change of the system.

For $\eta = 1$, either $T_1 = 0$ or $T_2 = \infty$, which is impossible. Therefore, efficiency of Carnot cycle cannot be 1. Therefore, total work done in the cyclic process will always be less that total heat.

Among all the cyclic processes operating between the given temperatures, efficiency of Carnot cycle is the maximum. Thus, we have the Clausius statement for the second law of thermodynamics, which states that: "It is impossible to have a cyclic process that converts the complete heat energy into work without some heat loss (q_{sink}) when some heat is transferred from body at higher temperature to body at lower temperature".

Solved Example 7-43

An inventor claims to have constructed an engine that has an efficiency of 75% when operated between the boiling and freezing points of water. Is this possible?

Solution

The efficiency of a real engine must be less than the efficiency of a Carnot engine operating between the same two temperatures.

The efficiency of a Carnot engine operating between the boiling and freezing points of water is

$$\eta = 1 - \frac{T_L}{T_H} = 1 - \frac{(0+273)\,\text{K}}{(100+273)\,\text{K}} = 0.268 \approx 27\%.$$

Thus, for the given temperatures, the claimed efficiency of 75% for a real engine (with its irreversible processes and wasteful energy transfers) is impossible.

Solved Example 7-44

Two moles of a perfect gas undergo the following processes:

(I) a reversible isobaric expansion from (1 atm, 20 L) to (1 atm, 40 L)

(II) a reversible isochoric change of state from (1 atm, 40 L) to (0.5 atm, 40 L)

(III) a reversible isothermal compression from (0.5 atm, 40 L) to (1 atm, 20 L)

- **(a)** Sketch with labels each of the processes on the same p–V diagram.
- **(b)** Calculate the total work (w) and the total heat change (q) involved in the above processes.
- **(c)** What will be the values of ΔU, ΔH and ΔS for the overall process? **(IIT-JEE 2002)**

Solution

(a) The graph is shown in Fig. 7.25

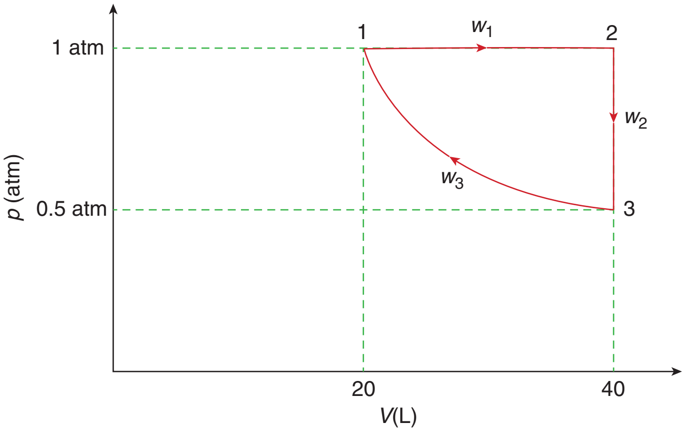


Figure 7.25

(b) $w_{\text{Total}} = w_1 + w_2 + w_3 = -p\Delta V + 0 + 2.303\,RT \log \frac{V_2}{V_1}$

$$= -1 \times 20 + 2.303 \times 2 \times 0.0821 \times 121.93 \log 2$$

$$= -6.13 \text{ L atm}$$

The process is cyclic, so $\Delta U = 0$. Now, $\Delta U = q + w$ (from first law of thermodynamics). So,

$$q = -w = +620.7 \text{ J}$$

(c) $\Delta S = 0$, $\Delta H = 0$ and $\Delta U = 0$ (cyclic process).

7.17 | ENTROPY AND SPONTANEITY

Let us understand the driving force for the processes where the enthalpy change is not favorable for the process to proceed spontaneously. We have seen that some endothermic reactions are spontaneous; now consider a process where enthalpy change is zero. Consider a partitioned closed container, with gases A and B, respectively, in each compartment. When the partition is removed, the molecules of both the gases diffuse and the resulting state of the system is more random than the starting state. Both parts of the container can contain molecules of gases A and B. We know that diffusion of gases is a spontaneous process, so the driving force of the process can be postulated as the tendency of the system to become more disordered or random (Fig. 7.26).

This leads to a new thermodynamic function called **entropy**, which is commonly considered to be a measure of disorder or randomness. Water molecules in the rigid structure in ice, for example, are more ordered than the water molecules moving about randomly in liquid water. The melting of ice, therefore, produces an increase in entropy. The increased freedom of motion of water in the liquid state means that liquid water has higher entropy than solid water.

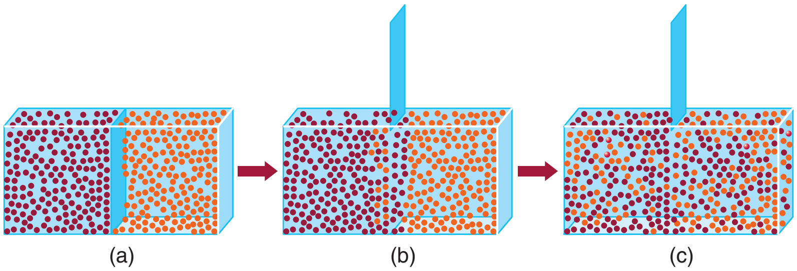


Figure 7.26 (a) partitioned closed container, with gases A and B. (b) Removal of partition causing diffusion of molecules. (c) Container containing both molecules A and B.

To see how entropy can affect the direction in which a process is spontaneous, consider the following experiments. Imagine that an ice cube is dropped into one beaker of water at room temperature at the same time that a red-hot coin is dropped into another beaker of water. The first law of thermodynamics tells us that changes in the energy of the ice cube and coin will be balanced by changes in the energy of the water. However, the first law does not tell us which substance loses energy and which gains energy. Experience, on the other hand, tells us that the water in the beaker with the ice cube will become cooler and the water in the beaker with the coin will become hotter.

At the moment the ice cube is dropped into the water, the temperature of the ice cube is lower than that of the water that surrounds it. Thus, the average kinetic energy of the molecules in the ice cube is significantly smaller than the average kinetic energy of the molecules in the water. During the melting of the ice cube, the rigid structure of the ice breaks down. After the ice cube melts, the average kinetic energy of the H_2O molecules is the same throughout the system, which is another way of stating that the temperature becomes uniform.

The exchange of energy between the ice cube and water has occurred in such a way that, after the ice cube melts, the spreading of energy has produced more disorder in the universe. The colder water molecules of ice have been warmed and released from the solid structure, thus becoming more disordered. The warmer molecules of liquid water have cooled and become more ordered. Overall, though, there is more disorder due to the breakup of the solid than there is order from the cooling of the warm water.

A similar process is at work when a red-hot coin is dropped into a beaker of water. Initially, the average kinetic energy of the atoms in the metal is significantly larger than the average kinetic energy of the molecules in the water. Eventually, the coin and the water that surrounds it will reach the same temperature. The coin cools, the water warms, there are more ways for the energy to be shared, and the universe has gone to a more disordered state.

Note: The reverse process in which the coin becomes warmer and the water colder does not occur because that process would result in a more ordered universe. The atoms in the hot coin would have had to acquire more order in warming, while the cold water molecules would have had to become more random (disordered) due to cooling.

Because neither of these processes could occur unless a net increase in the disorder of the universe occurred, we can conclude that these colder objects produce more disorder when brought to a common temperature than do the warmer objects. In other words, there is a total gain in disorder produced by the melting of the ice or the cooling of the coin.

In chemistry, we usually deal with systems that contain very large number of particles and it is usually impractical to count the number of ways that the particles can be arranged to produce a system with a particular energy. This can be done by a statistical method, which is beyond the scope of coverage. In a simpler method, the entropy of the system can be related to experimental heat and temperature measurements.

Like enthalpy, entropy is a state function. It depends only on the state of the system, so an **entropy change**, ΔS, is independent of the path from start to finish. As with other thermodynamic quantities, ΔS is defined as "final minus initial" or "products minus reactants." Thus,

$$\Delta S = S_{\text{final}} - S_{\text{initial}}$$

or for a chemical system,

$$\Delta S = S_{\text{products}} - S_{\text{reactants}}$$

As you can see, when S_{final} is larger than S_{initial} (or when S_{products} is larger than $S_{\text{reactants}}$), the value of ΔS is positive. A positive value for ΔS means an increase in the number of energy-equivalent ways the system can be produced, and we have seen that this kind of change tends to be spontaneous.

We know that when a system heated, the molecular motion of particles increases and so the randomness, and hence the entropy is expected to increase. At higher temperatures, the state of disorder in molecules is also higher than at lower temperatures. We also know that when heat is added to a system at lower temperature, the randomness increases to a greater extent than it does when the heat is added at higher temperature. These observations suggest that the disorder in particles in a system is directly proportional to the heat, and inversely proportional to the temperature. A small differential change in entropy is given by

$$\mathrm{d}S = \frac{\mathrm{d}q}{T}$$

where $\mathrm{d}q$ is the infinitesimal quantity of heat absorbed under reversible conditions at absolute temperature T. A finite change in entropy can be given by

$$\Delta S = \frac{q_{\text{rev}}}{T} \tag{7.31}$$

When heat is absorbed, q is positive and ΔS is also positive indicating an increase in entropy of the system.

In case of an isolated system, total entropy change is considered which is the sum total of entropy of system and surroundings.

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surrondings}} \tag{7.32}$$

For a change to be spontaneous, the final state should have greater randomness, and hence greater entropy than the initial state, therefore, $\Delta S_{\text{total}} > 0$; for a reversible or equilibrium process, $\Delta S_{\text{total}} < 0$. The conditions for spontaneity may also be defined considering the system alone. For a system in thermal equilibrium with its surroundings or undergoing reversible change, $\Delta S_{\text{total}} = 0$.

If the system undergoes an irreversible change, then in absence of any change in internal energy or volume, all spontaneous processes will result in increase in entropy. Thus, the change in entropy for reversible and irreversible systems will be different. The entropy changes can also be calculated for reversible and irreversible expansion in an isolated ideal gas system, on mixing of ideal gases and accompanying phase changes.

Calculation of ΔS for Different Processes

1. For an ideal gas (not undergoing physical or chemical change) in a reversible process.

$$\Delta S = \int \frac{\mathrm{d}q_{\text{rev}}}{T}$$

$$\Delta S = \int \frac{\mathrm{d}U - W}{T}$$

$$\Delta S = \int \frac{dU + p dV}{T} \qquad \text{(as } w = -pdV \text{ for reversible process)}$$

$$\Delta S = \int_{T_1}^{T_2} \frac{nC_V dT}{T} + \int_{V_1}^{V_2} \frac{nR}{V} dV$$

$$= nC_V \ln\left(\frac{T_2}{T_1}\right) + nR\ln\left(\frac{V_2}{V_1}\right)$$

Similarly $\Delta S = nC_p \ln\left(\frac{T_2}{T_1}\right) + nR\ln\left(\frac{p_1}{p_2}\right)$

2. For a real gas (not undergoing physical or chemical change)

(a) At constant pressure

$$\Delta S = nC_p \ln\left(\frac{T_2}{T_1}\right)$$

(b) At constant volume

$$\Delta S = nC_V \ln\left(\frac{T_2}{T_1}\right)$$

3. For a solid or liquid (not undergoing any physical or chemical change)

$$\Delta S = \int \frac{dU}{T} \ \text{(as } w \cong 0\text{)}$$

$$= \int_{T_1}^{T_2} \frac{nCdT}{T}$$

$$\Delta S = nC\ln\left(\frac{T_2}{T_1}\right) \quad \text{or} \quad ms\ln\left(\frac{T_2}{T_1}\right)$$

4. Calculation of $\Delta S_{\text{surroundings}}$

Consider the thermodynamic system and surrounding as shown in Fig. 7.27.

If system absorbs heat = q_{system}, the surroundings will give heat = $-q_{\text{system}}$ and vice versa. (Because for surroundings, we can assume all processes are reversible.) Therefore,

$$\Delta S_{\text{surrounding}} = \frac{-q_{\text{system}}}{T}$$

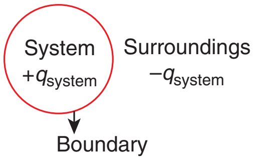


Figure 7.27 System and surroundings.

(a) Clausius inequality: It states that *Energy of universe is constant, but entropy of universe is ever increasing*. Thus

$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$

$\Delta S_{\text{universe}} \geq 0$ (Equality holds when process is reversible.)

$\Delta S_{\text{universe}} > 0$ (For an irreversible spontaneous process.)

$\Delta S_{\text{universe}} = 0$ (For a reversible process.)

$\Delta S_{\text{universe}} < 0$ (For an irreversible non spontaneous process.)

(b) Entropy change during mixing of gases

Consider the case of mixing of gas A and gas B (Fig. 7.28) at temperature T, such that volume of gases is V_1 and V_2, respectively and the number of moles are n_1 and n_2.

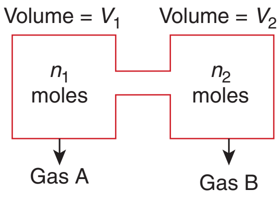


Figure 7.28 Mixing of two gases.

Then entropy of gas A is

$$\Delta S_A = nR\ln\left(\frac{V_1 + V_2}{V_1}\right)$$

And entropy of gas B is

$$\Delta S_B = nR\ln\left(\frac{V_1+V_2}{V_2}\right)$$

Therefore, $\Delta S_{\text{total}} = \Delta S_A + \Delta S_B > 0$.

Solved Example 7-45

1 mole of an ideal gas is subjected to a change from 10 atm to 1 atm at 300 K. Calculate ΔS_{system}, $\Delta S_{\text{surrounding}}$ and $\Delta S_{\text{universe}}$ if processes are carried out

(a) reversibly

(b) irreversibly

(c) during free expansion

Solution

(a) $\Delta S_{\text{system}} = nC_p\ln\left(\frac{T_2}{T_1}\right) + nR\ln\left(\frac{p_1}{p_2}\right)$

Given that $T_1 = T_2 = 300$, $p_1 = 10$ and $p_2 = 1$ and $n = 1$. Therefore,

$$\Delta S_{\text{system}} = R\ln 10$$

$$\Delta S_{\text{universe}} = 0 \text{ (reversible process)}$$

Thus, $\Delta S_{\text{surrounding}} = -R\ln 10$

(b) In case an isothermal process is carried out reversibly or irreversibly, ΔS_{system} is the same as it is a state function and initial and final states are the same. Therefore,

$$\Delta S_{\text{system}} = R\ln 10$$

$$q = -w = -1\left(\frac{R(300)}{1} - \frac{R(300)}{10}\right) = +270\ R$$

Therefore,

$$\Delta S_{\text{surrounding}} = \frac{-q}{T_{\text{surrounding}}} = \frac{-270R}{300} = \frac{-9R}{10}$$

$$\Delta S_{\text{universe}} = R\ln 10 - \frac{9R}{10} > 0$$

(c) $\Delta S_{\text{system}} = R\ln 10$

For an isothermal process $q = 0$ and $\Delta S_{\text{surrounding}} = 0$. Therefore,

$$\Delta S_{\text{universe}} = R\ln 10 > 0$$

Factors Affecting Entropy

Several factors influence the magnitude of the entropy in predictable ways, so it is often possible to predict whether ΔS is positive or negative for a particular change. These factors are listed as follows.

1. **Volume changes:** For gases, the entropy increases with increasing volume. The gas expands spontaneously to achieve a more probable (higher entropy) particle distribution.
2. **Temperature changes:** The higher the temperature, the larger is the entropy. If some heat is added to the solid, the kinetic energy of the particles increases along with the temperature. This causes the particles to move and vibrate within the crystal. There is more kinetic energy than at the lower temperature, and there are more ways to distribute it among the molecules, so the entropy is larger. If the temperature is raised further, the particles are given even more kinetic energy with an even larger number of possible ways to distribute it, causing the solid to have still higher entropy.
3. **Physical state:** In general, there are many more possible ways to distribute kinetic energy among gas molecules than there are in liquids and solids. Therefore, a gas has a much larger entropy compared to a liquid or solid. These changes which produce gases from liquids or solids are almost always accompanied by increases in entropy.
4. **Number of particles:** As the number of particles increases, the number of ways of distributing energy also increases, and hence, entropy increases.
5. If number of gaseous moles increase in a chemical reaction or $\Delta n_g > 0$ then $\Delta S > 0$, only in reactions involving gases.

Solved Example 7-46

For the following changes predict if ΔS is positive, 0 or negative.

(a) $\underset{\text{(ice)}}{H_2O} \rightarrow \underset{\text{(liquid)}}{H_2O}$

(b) $\underset{\text{(raw)}}{\text{Egg}}\ ^{\circ}\ \underset{\text{(boiled)}}{\text{Egg}}$

(c) $\underset{\text{(white)}}{\text{P}}\ ^{\circ}\ \underset{\text{(Red)}}{\text{P}}$

(d) $\underset{\text{(diamond)}}{\text{C}}\ ^{\circ}\ \underset{\text{(graphite)}}{\text{C}}$

Solution

(a) Ice has cage like structure, so less randomness and liquid water has more randomness, therefore, $\Delta S > 0$.

(b) Raw egg is liquid but has a long change of amino acids (proteins). Boiled egg is solid but constitute of much smaller molecules. Therefore, $\Delta S > 0$.

(c) White phosphorus is made up of small molecules, whereas red phosphorus has long chain polymeric structure. Therefore, $\Delta S < 0$

(d) Diamond has three-dimensional network structure whereas graphite has two-dimensional layer structure in which layers are held by weak van der Waal forces. Diamond has less randomness than graphite, therefore, $\Delta S > 0$.

Entropy of Physical Changes

All physical changes are accompanied by a change in entropy and are defined as follows.

1. **Entropy of fusion:** It is the increase in entropy when a solid substance melts at its melting point. It is always a positive value because melting results in an increase in randomness. It is denoted by ΔS_{fusion} and is expressed as

$$\Delta S_{\text{fusion}} = S_{\text{liquid}} - S_{\text{solid}} = \frac{\Delta H_{\text{fusion}}}{T_{\text{m}}}$$

where T_{m} is the melting point of the solid.

2. **Entropy of vaporization:** It is the increase in entropy when a liquid substance vaporizes at its boiling point. It is always a positive value because vaporization always results in an increase in randomness.
It is denoted by ΔS_{vap} and expressed as

$$\Delta S_{\text{vap}} = S_{\text{vapor}} - S_{\text{liquid}} = \frac{\Delta H_{\text{vap}}}{T_{\text{b}}}$$

where T_{b} is the boiling point of the liquid. An empirical observation, called the **Trouton's rule**, states that a wide range of liquids have approximately the same standatard entropy of vaporization (~85 kJ mol^{-1}) at their boiling points.

3. **Entropy of sublimation:** It is the increase in entropy when a solid substance converts directly into vapor at any temperature, that is, sublimation of a solid takes place. It is always a positive quantity because sublimation results in increase in randomness. It is denoted by ΔS_{sub} and is expressed as

$$\Delta S_{\text{sub}} = S_{\text{vapor}} - S_{\text{solid}} = \frac{\Delta H_{\text{sub}}}{T}$$

Entropy of Chemical Changes

The entropy change accompanying a chemical reaction is given by the difference between the sum of entropies of all products and sum of entropies of all reactants. For any chemical reaction:

$$\text{A} + \text{B} \rightarrow \text{C} + \text{D}$$

the entropy change is given by

$$\Delta S = (S_{\text{C}} + S_{\text{D}}) - (S_{\text{A}} + S_{\text{B}})$$

where S_A, S_B, S_C, S_D are entropies of the pure substances used as reactants and formed as products. For any chemical reaction in general, the entropy change is given by

$$\Delta S = \sum S_{\text{products}} - \sum S_{\text{reactants}} \tag{7.33}$$

The entropy of a substance at 25°C (298 K) and 1 atm pressure is called the standard entropy of the substance and is represented as $S°$. In a chemical reaction, if all the reactants and products are in standard state, then the entropy change for the reaction is said to be standard entropy change and is expressed as

$$\Delta S^{\circ} = \Sigma S^{\circ}_{\text{products}} - \Sigma S^{\circ}_{\text{reactants}}$$

Variation of Entropy Change for a Reaction with Temperature and Pressure

1. **At constant pressure:** We know that at constant pressure, entropy varies with temperature as

$$S_{T_2} - S_{T_1} = \int_{T_1}^{T_2} nC_p \mathrm{d}T$$

For the reaction

$$aA + bB \rightarrow cC + dD$$

$$\Delta S_{\text{reaction}} = cS_C + dS_D - aS_A - bS_B$$

$$\Delta S_{T_2} - \Delta S_{T_1} = \int_{T_1}^{T_2} \frac{[c(C_{p,C} + d(C_{p,D}) - a(C_{p,A}) - b(C_{p,B})]\mathrm{d}T}{T}$$

$$\Delta S_{T_2} - \Delta S_{T_1} = \int_{T_1}^{T_2} (\Delta C_p)_{\text{reaction}} \frac{\mathrm{d}T}{T} = (\Delta C_p)_{\text{reaction}} \ln\left(\frac{T_2}{T_1}\right)$$

(If ΔC_p is independent of T.)

2. **At constant temperature (for gases only):**

$$S_{p_2} - S_{p_1} - \int_{p_1}^{p_2} nR\mathrm{d}p$$

$$\Delta S_{p_2} - \Delta S_{p_1} = \Delta n_g R \ln\left(\frac{p_1}{p_2}\right)$$

Note: Entropy of solids and liquids do not change with pressure.

Solved Example 7-47

(a) When a teaspoon of table salt is poured into a glass of water, the salt dissolves, even though heat is absorbed during the process. Is this a spontaneous process?

(b) Predict the sign of the entropy change for the condensation of steam to liquid water and the sublimation of a solid.

Solution

(a) Dissolving salt in water is a spontaneous process. Even though heat is absorbed during the process, the salt dissolves because the system (water and salt) becomes more disordered as the salt dissolves.

(b) The sign of entropy change will be negative for the condensation of steam to liquid water because entropyis larger in the gaseous state as compared to the liquid state. For sublimation of solid, when the system will change from solid to gas, the disorder in the system will increase and hence the sign for entropy change will be positive.

Solved Example 7-48

Nitrogen dioxide, NO_2, an air pollutant, dissolves in rainwater to form a dilute solution of nitric acid. The equation for the reaction is

$$3NO_2(g) + H_2O(l) \rightarrow 2HNO_3(l) + NO(g)$$

Calculate ΔS° for the reaction in J K^{-1}.

Solution

The entropy change is given by

$$\begin{aligned}\Delta S^\circ &= \Sigma S^\circ(\text{products}) - \Sigma S^\circ(\text{reactants})\\ &= [2S^\circ(HNO_3(l)) + S^\circ(NO(g))] - [3S^\circ(NO_2(g)) \\ &\qquad + S^\circ(H_2O(l))]\end{aligned}$$

Substituting values, we get

$$\begin{aligned}\Delta S^\circ = {} & [2\,\text{mol} \times (155.6\,\text{J mol}^{-1}\,\text{K}^{-1}) + 1\,\text{mol} \times (210.6\,\text{J mol}^{-1}\text{K}^{-1})]\\ & -[3\,\text{mol} \times (240.5\,\text{J mol}^{-1}\text{K}^{-1}) + 1\,\text{mol} \times (69.96\,\text{J mol}^{-1}\text{K}^{-1})]\end{aligned}$$

Solving, we get $\Delta S^\circ = -269.7$ J K^{-1}.

Solved Example 7-49

What is the boiling point of a liquid with entropy of vaporization 68.3 J K^{-1} mol^{-1} and enthalpy of vaporization 35.65 kJ mol^{-1}?

Solution

For a phase transition, entropy change is given by

$$\Delta S = \frac{\Delta H}{T}$$

For vaporization, $$\Delta S = \frac{\Delta_{\text{vap}} H}{T}$$

where T is the boiling point of the substance on Kelvin scale. Given that $\Delta S = 68.3$ J K^{-1}; $\Delta H = 35.65$ kJ mol^{-1} = 35650 J mol^{-1}. Substituting values in the above equation, we get

$$68.3 = \frac{35650}{T}$$

or $$T = \frac{35650}{68.3} = 521.96\ \text{K} = 521.96 - 273 = 248.96^\circ\text{C}$$

The boiling point of the liquid is 248.96°C.

Solved Example 7-50

Predict the sign of ΔS for the following reactions. Justify your answers

(a) $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$

(b) $CO(g) + 2H_2(g) \rightarrow CH_3OH(g)$

(c) $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

(d) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

(e) $Ca(OH)_2(s) \xrightarrow{H_2O} Ca^{2+}(aq) + 2OH^-(aq)$

Solution

(a) ΔS is negative since there are less gas molecules. (The product is also more complex, indicating an increase in order.)

(b) ΔS is negative since there are less gas molecules. (The product is also more complex, indicating an increase in order.)

(c) ΔS is negative since there is a change from a gas phase to a liquid phase. (The product is also more complex, indicating an increase in order.)

(d) ΔS is negative since there are less gas molecules. (The product is also more complex, indicating an increase in order.)

(e) ΔS is positive since the particles go from an ordered, crystalline state to a more disordered, aqueous state.

7.18 | GIBBS ENERGY AND SPONTANEITY

We have learnt that the total entropy change of the system can predict the spontaneity, but calculation of ΔS_{total} would require consideration of both the system and the surroundings. Most of the chemical processes occur in closed or open systems which undergo both enthalpy and entropy changes. The spontaneity of a process will thus depend both on enthalpy as well as entropy change. A new thermodynamic function called **Gibbs energy** or Gibbs function was defined by J. Willard Gibbs. The Gibbs energy of a system at any moment in time is defined as the enthalpy of the system minus the product of the temperature times the entropy of the system.

$$G = H - TS$$

Gibbs energy is a state function because it is defined in terms of thermodynamic properties (enthalpy, entropy, and temperature) that are state functions. Therefore,

$$\Delta G = G_{\text{final}} - G_{\text{initial}}$$

For any system, the change in Gibbs energy can be expressed as

$$\Delta G_{\text{system}} = \Delta H_{\text{system}} - T\Delta S_{\text{system}} - S_{\text{system}}\Delta T$$

For a process at constant temperature, $\Delta T = 0$, therefore,

$$\Delta G_{\text{system}} = \Delta H_{\text{system}} - T\Delta S_{\text{system}}$$

At a given temperature, the change in the Gibbs energy of the system that occurs during a reaction is, therefore, equal to the change in the enthalpy of the system minus the product of the temperature times the change in entropy of the system.

$$\Delta G = \Delta H - T\Delta S \tag{7.34}$$

In the expression for Gibbs energy, both ΔH and $T\Delta S$ ($\text{K} \times \text{J K}^{-1} = \text{J}$), are energy terms, therefore, change of Gibbs energy has units of energy.

The change in Gibbs energy is determined by change in both enthalpy and entropy of the system and should thus be a suitable parameter to predict spontaneity of a process. Consider a system in thermal equilibrium with its surroundings, then the enthalpy loss by the system is equal to the enthalpy gain of the surroundings and the system and surroundings are maintained at the same temperature. The entropy change can be represented as

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \tag{7.35}$$

It can be shown that the entropy change for the surroundings is equal to the heat transferred *to* the surroundings *from* the system, $q_{\text{surroundings}}$, divided by the Kelvin temperature, T, at which it is transferred.

$$\Delta S_{\text{surroundings}} = \frac{q_{\text{surroundings}}}{T}$$

The law of conservation of energy requires that the heat transferred to the surroundings equals the negative of the heat added to the system, so we can write

$$q_{\text{surroundings}} = -q_{\text{system}}$$

The entropy change for the surroundings can be expressed in terms of enthalpy change as

$$\Delta S_{\text{surroundings}} = \frac{\Delta H_{\text{surroundings}}}{T} = -\frac{\Delta H_{\text{system}}}{T}$$

Substituting in Eq. (7.35), we get

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} - \frac{\Delta H_{\text{system}}}{T}$$

Rearranging, we get

$$T\Delta S_{\text{total}} = T\Delta S_{\text{system}} - \Delta H_{\text{system}}$$

For a spontaneous process, the total entropy change should be positive, that is $\Delta S_{\text{total}} > 0$, therefore,

$$T\Delta S_{\text{system}} - \Delta H_{\text{system}} > 0 \Rightarrow -(\Delta H_{\text{system}} - T\Delta S_{\text{system}}) > 0$$

Using Eq. (7.34), this relation can be expressed in terms of Gibbs energy change as

$$-\Delta G > 0 \Rightarrow \Delta G < 0$$

or

$$\Delta G = \Delta H - T\Delta S < 0$$

Thus, at constant temperature and pressure, a process is spontaneous if $\Delta G < 0$ and non-spontaneous if $\Delta G > 0$. *At constant temperature and pressure, a change can only be spontaneous if it is accompanied by a decrease in the Gibbs energy of the system.* In other words, for a change to be spontaneous, G_{final} must be less than G_{initial} and ΔG must be negative. With this in mind, we can now examine how ΔH, ΔS and T are related in determining spontaneity.

1. When ΔH is negative and ΔS is positive, the process is spontaneous.
2. When ΔH is positive and ΔS is negative, the process is not spontaneous.
3. When ΔH and ΔS have the same algebraic sign, the temperature becomes the determining factor in controlling spontaneity.
   (a) If ΔH and ΔS are both positive, then

$$\Delta G = (+) - [T(+)]$$

   Thus, ΔG is the difference between two positive quantities, ΔH and $T\Delta S$. This difference will only be negative if the term $T\Delta S$ is larger in magnitude than ΔH, and this will only be true when the temperature is high. In other words, when ΔH and ΔS are both positive, the change will be spontaneous at high temperature but not at low temperature. Melting of ice is an example.

   (b) Similarly, when ΔH and ΔS are both negative, ΔG will be negative (and the change spontaneous) only when the temperature is low.

$$\Delta G = (-) - [T(-)]$$

   Only when the negative value of ΔH is larger in magnitude than the negative value of $T\Delta S$, will ΔG be negative. Such a change is only spontaneous at low temperatures. An example is the freezing of water.

Using Eq. (7.34), the predictions about spontaneity of reaction can be summarized in Table 7.5.

Table 7.5 Criteria for spontaneity of physical and chemical processes

Enthalpy	Entropy	Gibbs Energy	Reaction
$\Delta H < 0$	$\Delta S > 0$	$\Delta G < 0$	Spontaneous
$\Delta H > 0$	$\Delta S < 0$	$\Delta G > 0$	Non-spontaneous
$\Delta H > 0$	$\Delta S > 0$	$\Delta G < 0$ at high temperature	Spontaneous at high temperature
		$\Delta G > 0$ at low temperature	Non-spontaneous at low temperature
$\Delta H < 0$	$\Delta S < 0$	$\Delta G < 0$ at low temperature	Spontaneous at low temperature
		$\Delta G > 0$ at high temperature	Non-spontaneous at high temperature

We know that in all real processes, the enthalpy change is not completely converted into work as some amount of heat is lost to the surrounding and used in overcoming opposing forces. In the expression for Gibbs energy, if ΔH corresponds to the enthalpy change for the system, then $T\Delta S$ corresponds to the energy not available for doing work and ΔG corresponds to energy available for doing useful work. Thus, Gibbs energy is a measure of free energy of the system so Gibbs energy change for the reaction is known as free energy of the reaction.

Note: Reactions that occur with a Gibbs energy decrease are sometimes said to be exergonic. Those that occur with a Gibbs energy increase are sometimes said to be endergonic.

Mathematical Derivation of ΔG

$$G = H - TS$$
$$G = U + pV - TS$$
$$\mathrm{d}G = \mathrm{d}U + p\mathrm{d}V + V\mathrm{d}p - T\mathrm{d}S - S\mathrm{d}T$$
$$\mathrm{d}G = \mathrm{d}q + w_{pV} + w_{\text{non-}pV} + p\mathrm{d}V + V\mathrm{d}p - T\mathrm{d}S - S\mathrm{d}T$$

where w_{pV} is pV work and $w_{\text{non-}pV}$ is non-pV work.

$$\mathrm{d}G = \mathrm{d}q - p\mathrm{d}V + W_{\text{non-}pV} + p\mathrm{d}V + V\mathrm{d}p$$

(Because $w_{pV} = -p\mathrm{d}V$.)

$$(\Delta G)_{T,p} = \mathrm{d}q + w_{\text{non-}pV} - T\mathrm{d}S$$

(Because pressure and temperature are constant.)

Assuming that non-pV work is zero, that is, $W_{\text{non-}pV} = 0$, we have

$$(\Delta G)_{T,p} = \mathrm{d}q - T\mathrm{d}S$$
$$\mathrm{d}S_{\text{surrounding}} = -\frac{\mathrm{d}q}{T}$$
$$(\Delta G)_{T,p} = -T(\mathrm{d}S_{\text{surrounding}} + \mathrm{d}S) = -T(\mathrm{d}S_{\text{universe}})$$

Therefore, $\mathrm{d}S_{\text{universe}} < 0 \Rightarrow \mathrm{d}G > 0$ (Non-spontaneous)
$\mathrm{d}S_{\text{universe}} > 0 \Rightarrow \mathrm{d}G < 0$ (Spontaneous)
$\mathrm{d}S_{\text{universe}} = 0 \Rightarrow \mathrm{d}G = 0$ (Reversible)

Solved Example 7-51

(a) Nitric oxide (NO) reacts with molecular oxygen as follows: $2\text{NO (g)} + \text{O}_2\text{ (g)} \rightarrow 2\text{ NO}_2\text{ (g)}$

Initially NO and O_2 are separated as shown in Fig. 7.29. When the valve is opened, the reaction quickly goes to completion. Determine what gases remains at the end of reaction and calculate their partial pressures. Assume that the temperature remains constant at 27°C. [Given: $R = 0.08$ atm L mol^{-1} K^{-1}.]

(b) Two moles of an ideal gas expand irreversibly and isothermally at 27°C until its volume doubled and 3.3 kJ heat is absorbed from surrounding. Determine ΔS_{system} and $\Delta S_{\text{surroundings}}$.

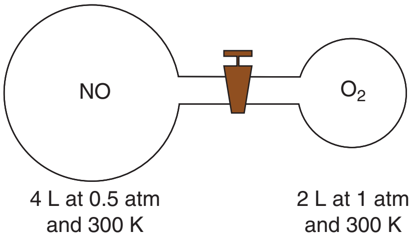


Figure 7.29

Solution

(a) The number of moles of each gas present initially is obtained using the relation $pV = nRT$. Therefore,

$$n_{\text{NO}} = \frac{0.5 \times 4}{0.080 \times 300},\ n_{\text{O}_2} = \frac{2 \times 1}{0.080 \times 300}$$

$$2\text{NO (g)} + \text{O}_2\text{ (g)} \rightarrow 2\text{ NO}_2\text{ (g)}$$

Initially	$\frac{2}{24.0}$	$\frac{2}{24.0}$	0
At the end of the reaction	$\frac{1}{24}$	$\frac{1}{24}$	$\frac{1}{12}$

NO_2 and O_2 gases remain at the end of reaction and $V_{\text{total}} = 6$ L

$$\text{Partial pressure of O}_2 = \frac{1}{24} \times \frac{0.080 \times 300}{6}$$
$$= \frac{1}{6} \text{ or } 0.166 \text{ atm}$$

$$\text{Partial pressure of } NO_2 = \frac{1}{12}\times\frac{0.080\times 300}{6}$$

$$= \frac{1}{3} \text{ or } 0.333 \text{ atm}$$

(b) $\Delta S_{\text{system}} = nR\ln\frac{V_2}{V_1} \Rightarrow 2\times \mathrm{R}\times \ln 2 = 11.52 \text{ J K}^{-1}$

$$\Delta S_{\text{surroundings}} = \frac{q_{\text{surroundings}}}{T} = \frac{-q_{\text{system}}}{T}$$

$$= \frac{-3.3\times 1000}{300} = -11 \text{ J K}^{-1}$$

Solved Example 7-52

Show that the reaction $CO(g) + \frac{1}{2}O_2\ (g) \rightarrow CO_2(g)$ at 300 K is spontaneous and exothermic, when the standard entropy change is – 0.094 kJ mol^{-1} K^{-1}. the standard Gibbs free energies of formation for CO_2 and CO are –394.4 and –137.2 kJ mol^{-1}, respectively. **(IIT-JEE 2000)**

Solution

For the reaction $CO(g)+\frac{1}{2}O_2 \rightarrow CO_2(g)$, Gibbs energy change is given by

$$\Delta_r G^o = \Delta G^o_{CO_2} - \left(\Delta G^o_{CO} + \frac{1}{2}\Delta G^o_{O_2}\right)$$

$$= -394.4 - \left(-137.2 \times \frac{1}{2}\times 0\right) = -257.2 \text{ kJ mol}^{-1}$$

Substituting values and solving, we get

$\Delta G^o = \Delta H^o - T\Delta S^o$ where $\Delta H^\circ = -285.4$ kJ mol^{-1}

Since, ΔH° = negative, exothermic; ΔG° = negative. So, the reaction is spontaneous

Solved Example 7-53

Determine whether the following reaction (equation unbalanced) will be spontaneous at 25°C.

$$C_2H_4(g) + HNO_3(l) \rightarrow CH_3COOH(l) + H_2O(l) + NO(g) + NO_2(g)$$

Solution

The reaction is spontaneous if its associated value for ΔG° is negative.

$$\Delta G^o = \Sigma\Delta_f G^o(\text{products}) - \Sigma\Delta_f G^o(\text{reactants})$$

$$= \{\Delta_f G^o[CH_3COOH(l)] + \Delta_f G^\circ[H_2O(l)] + \Delta_f G^\circ[NO(g)] + \Delta_f G^\circ[NO_2(g)]\} - \{\Delta_f G^o[C_2H_4(g)] + \Delta_f G^o\ [HNO_3(l)]\}$$

Substituting the values of heat of formation of compounds from Table 7.3, we have

$$\Delta G^o = \{1 \text{ mol}\times(-392.5 \text{ kJ mol}^{-1}) + 1 \text{ mol}\times(-237.2 \text{ kJ mol}^{-1}) + 1 \text{ mol}\times(86.69 \text{ kJ mol}^{-1}) + 1 \text{ mol}\times(51.84 \text{ kJ mol}^{-1})\} - \{1 \text{ mol}\times(68.12 \text{ kJ mol}^{-1}) + 1 \text{ mol}\times(-79.91 \text{ kJ mol}^{-1})\}$$

$$= -479.4 \text{ kJ}$$

Since ΔG^o is negative, so the reaction is spontaneous.

7.19 | SECOND LAW OF THERMODYNAMICS

We have learnt about the limitations of the first law of thermodynamics. It tells us that energy would be conserved in any process and the law is always obeyed when a process takes place either on its own or by help of an external force. It establishes relation between heat and work and indicates the possibility of complete conversion of heat into mechanical work. However, experience shows that heat cannot be completely converted into mechanical work.

The first law also does not give any information about the feasibility and extent of the reaction. We have learnt that the thermodynamic function entropy is a measure of randomness of the system and is the driving force for irreversible processes to occur spontaneously. For irreversible processes, the total entropy, that is, the entropy of the system and surroundings taken together, increases for all spontaneous processes and remains constant for a process at equilibrium. These observations lead to the statement of the **second law of thermodynamics**, which states, in effect, that *whenever a spontaneous event takes place in our universe, the total entropy of the universe increases* ($\Delta S_{\text{total}} > 0$). Notice that the increase in entropy that is referred to here is for the *total* entropy of the *universe* (system *plus* surroundings), not just the system alone. This means that a system's entropy can decrease, just as long as there is a larger increase in the entropy of the surroundings so that the *overall* entropy change is positive.

Since all natural processes are spontaneous and irreversible, they are accompanied by a net increase in entropy. So the second law of thermodynamics was also stated by Clausius as *"the entropy of the universe tends always to a maximum". The statement for second law essentially implies that for entropy change in universe*,

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

The spontaneity of the process can be predicted on the basis of the following

If $\Delta S_{\text{universe}} > 0$, the reaction is spontaneous.
If $\Delta S_{\text{universe}} < 0$, the reaction is non-spontaneous.
If $\Delta S_{\text{universe}} = 0$, the reaction is at equilibrium.

In chemistry, we are interested in the spontaneity of chemical reactions and physical changes in systems. Thus, we would look for criteria for predicting the spontaneity of the changes in the system rather than the surroundings. We have seen that the driving force that is responsible for spontaneity of process may be discussed in terms of Gibbs energy change ($\Delta G = \Delta H - T\Delta S$). The second law of thermodynamics can be stated in terms of Gibbs energy as that in any spontaneous process, at constant temperature and pressure, the Gibbs energy of the system (ΔG_{system}) always decreases. So, the spontaneity of a process can be predicted on the basis of the following

If $\Delta G_{\text{system}} > 0$, the reaction is spontaneous.
If $\Delta G_{\text{system}} < 0$, the reaction is non-spontaneous.
If $\Delta G_{\text{system}} = 0$, the reaction is at equilibrium.

7.20 | GIBBS ENERGY CHANGE AND EQUILIBRIUM

In the previous section, we have seen in a chemical reaction,

1. The sign of Gibbs energy is useful in predicting the spontaneity of reaction.
2. The magnitude of the Gibbs energy change for a reaction is useful to predict the useful work that could be extracted from it.

From the first law of thermodynamics, the total heat energy supplied to the system changes the internal energy of the system, causes expansion of gas (pressure–volume work) and is converted into useful work. This is represented as:

$$q = \Delta U + w_{\text{pressure-volume work}} + w_{\text{useful work}} = \Delta U + p\Delta V + w_{\text{useful work}}$$

$$q = \Delta H + w_{\text{useful work}} \qquad (7.36)$$

Since, $$q = T\Delta S \qquad (7.37)$$

Using Eqs. (7.36) and (7.37), we get

$$T\Delta S = \Delta H + w_{\text{useful work}}$$

or $$\Delta H - T\Delta S = -w_{\text{useful work}}$$

or $$-(\Delta G)_{p,T} = w_{\text{useful work}} \qquad (7.38)$$

Equation (7.38) shows that the decrease in Gibbs energy during a thermodynamic process is equal to the useful work obtainable from the system.

The above criteria are applicable for irreversible processes. Let us now examine the Gibbs energy changes for reversible processes. We have seen that a reversible process is such that at each state the system is at equilibrium with the surroundings. When applied to chemical reactions, it implies that the reactants and products are at dynamic equilibrium and can proceed in either direction with decrease in Gibbs energy. Such a state is only possible if the Gibbs energy at equilibrium is at a minimum or $\Delta_r G = 0$.

The Gibbs energy change for a system when the process is carried out at 25°C (298 K) and 1 atm pressure is called standard Gibbs energy change (ΔG°). Thus, if for a chemical reaction, reactants in their standard state are converted into products in their states, the standard Gibbs energy change is given by

$$\Delta G^{\circ} = \Sigma G^{\circ}_{\text{products}} - \Sigma G^{\circ}_{\text{reactants}} \tag{7.39}$$

Quantitatively, the relationship between $\Delta_r G$ and ΔG° for a reaction is expressed by the following equation,

$$\Delta_r G^{\circ} = \Delta G^{\circ} + RT\ln Q \tag{7.40}$$

where R is the gas constant in appropriate energy units (e.g., 8.314 J mol^{-1} K^{-1}), T is the Kelvin temperature, and ln Q is the natural logarithm of the reaction quotient. For gaseous reactions, Q is calculated using partial pressures expressed in atm; for reactions in solution, Q is calculated from molar concentrations.

We have learnt that when a system reaches equilibrium the Gibbs energy of the products equals the Gibbs energy of the reactants and $\Delta_r G$ equals zero. We also know that at equilibrium, the reaction quotient equals the equilibrium constant.

$$\text{At equilibrium}\begin{cases}\Delta_r G = 0\\ Q = K\end{cases}$$

If we substitute these into Eq. (7.40), we obtain

$$0 = \Delta G^{\circ} + RT\ln K$$

which can be rearranged to give

$$\Delta_r G^{\circ} = -RT\ln K = -2.303RT\log K \tag{7.41}$$

Using expression for Gibbs energy, we can relate equilibrium constant to enthalpy change and entropy as

$$\Delta_r G^{\circ} = \Delta_r H^{\circ} - T\Delta_r S^{\circ} = -RT\ln K = -2.303RT\log K \tag{7.42}$$

Some important implications of the above relations are:

1. For strongly endothermic reactions, the value of $\Delta_r H^{\circ}$ is large and positive, so the value of equilibrium constant is much smaller than 1 and the reaction does not proceed to a great extent towards formation of products.
2. For strongly exothermic reactions, the value of $\Delta_r H^{\circ}$ is large and negative, so value of equilibrium constant will be much larger than 1 and the reaction would proceed towards completion.
3. The value for $\Delta_r G^{\circ}$ also depends on the changes of entropy ($\Delta_r S^{\circ}$) accompanying the reaction, so the value of equilibrium constant will be affected by whether the entropy change is positive or negative.
4. Using Eq. (7.42), if we can determine the Gibbs energy change for the reaction by measuring $\Delta_r H^{\circ}$ and $\Delta_r S^{\circ}$, it is possible to estimate the equilibrium constant at any temperature and estimate the possible yield of the reaction.
5. If the equilibrium constant for the reaction can be determined in the laboratory, then it can be used to calculate the value of $\Delta_r G^{\circ}$ at any temperature using Eq. (7.42).

Calculation of ΔG

The calculation of ΔG for different cases is discussed as follows.

1. For a substance (not undergoing any chemical or phase change) under reversible condition.

$$\mathrm{d}G = \mathrm{d}U + p\mathrm{d}V + V\mathrm{d}p - T\mathrm{d}S - S\mathrm{d}T$$

$$\mathrm{d}U = q + w = T\mathrm{d}S - p\mathrm{d}V$$

$$\mathrm{d}G = V\mathrm{d}p - S\mathrm{d}T \tag{7.43}$$

Simplification of Eq. (7.43)

(a) An ideal gas at constant temperature

$$\mathrm{d}G = V\mathrm{d}p = \frac{nRT}{p}\mathrm{d}p$$

$$\Delta G = nRT\ln\left(\frac{p_2}{p_1}\right)$$

(b) For solids/liquids at constant temperature

$$dG = Vdp$$
$$\Delta G = V(p_2 - p_1)$$

(i) $\left(\frac{\partial G}{\partial T}\right)_p = -S$

Therefore, slope of G vs. T graph gives – S

(ii) $\left(\frac{\partial G}{\partial p}\right)_T = V$

Therefore, slope of G vs. p graph gives V.

(iii) For any chemical reaction

$$aA + aB \,^{\circ}\; cC + dD$$

$$\Delta_r G = \Delta_r H - T\Delta_r S \tag{7.44}$$

where, $\Delta_r G$ = Gibbs free energy change of the reaction
$\Delta_r H$ = Enthalpy of reaction
$\Delta_r S$ = Enthalpy change of the reaction

Variation of the Equation 7.44

(a) At constant pressure

$$(\Delta_r G)_{T_2} = (\Delta H)_{T_2} - T_2(\Delta S)_{T_2}$$

Therefore,

$$(\Delta_r G)_{T_2} = (\Delta H)_{T_1} + (\Delta C_p)_r(T_2 - T_1) - T_2\left((\Delta S)_{T_1} + (\Delta C_p)_r \ln\frac{T_2}{T_1}\right)$$

(Derived before !!)

(b) At constant temperature

$$(\Delta_r G)_{p_2} = (\Delta H)_{p_2} - T_2(\Delta S)_{p_2}$$
$$(\Delta_r G)_{p_2} = (\Delta H)_{p_2} - T_2\left((\Delta S)_{T_1} + \Delta n_g R\ln\left(\frac{p_1}{p_2}\right)\right)$$

(Derived before !!)

Solved Example 7-54

For the following reaction

$$\underset{(1\text{ atm, }373\text{ K})}{H_2O} \rightarrow \underset{(1\text{ atm, }373\text{ K})}{H_2O}$$

$\Delta H = 40$ kJ/mol
$C_p\,(H_2O, l) = 40$ J/mol K
$C_p\,(H_2O, g) = 30$ J/mol K

Then calculate ΔG at

(a) 1 atm, 373 K
(b) 1 atm, 300 K

Solution

(a) Since 373 K is the boiling point of H_2O (l), therefore, the reaction is at equilibrium at 373 K. So

$$\Delta G\ (1\ \text{atm}, 373\ \text{K}) = 0$$

(b) We know that

$$\Delta H_{T_2} = \Delta H_{T_1} + \Delta C_p(T_2 - T_1)$$

Substituting values, we have

$$\Delta H_{300} = \Delta H_{373} + [30-40]\,[300-373]$$

$$= 40 \times 10^3 + (-10)\,(-73) = 40730\ \text{J mol}^{-1}$$

$$\text{Also, } \Delta S_{T_2} = \Delta S_{T_1} + \Delta C_p \ln\left(\frac{T_2}{T_1}\right)$$

Substituting values, we get

$$\Delta S_{300} = \Delta S_{373} + (-10)\ln\left(\frac{300}{373}\right)$$

$$\text{Now, } \Delta S_{373} = \frac{\Delta H_{373}}{373} = \frac{40\times 10^3}{373}$$

Therefore,

$$\Delta S_{300} = \frac{40\times 10^3}{373} - 10\ln\left(\frac{300}{373}\right)$$

$$= 107.238 + 2.177 = 109.415\ \text{J mol}^{-1}\text{K}^{-1}$$

Thus,

$$\Delta G_{300} = \Delta H_{300} - 300\ (\Delta S_{300})$$

$$= 40730 - 300\ (109.415) = 73544.5\text{J mol}^{-1}$$

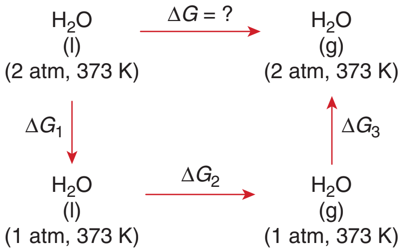
Solved Example 7-55

Calculate ΔG for the following reaction

$$\underset{(2\ \text{atm},\ 373\ \text{K})}{H_2O} \rightarrow \underset{(2\ \text{atm},\ 373\ \text{K})}{H_2O}$$

Solution

Since ΔG is a state function, therefore, we can write the above equation as



Therefore, $\Delta G = \Delta G_1 + \Delta G_2 + \Delta G_3$

$$dG_1 = Vdp - SdT = V_1 dp \quad (\text{as } T \text{ is constant})$$

Therefore, $\Delta G_1 = V_1(p_2 - p_1)$

$$\Delta G_2 = 0\ (\text{at equilibrium})$$

$$\Delta G_3 = nRT\ln\frac{p_2}{p_1}$$

Thus,

$$\Delta G = V_1(p_2 - p_1) + nRT\ln\frac{p_2}{p_1}$$

Note: On changing pressure, always use $dG = Vdp$. Do not use $\Delta G = \Delta H - T\Delta S$, as ΔH is unknown at other pressures.

Gibb's Helmholtz Equation

We have

$$dG = Vdp - SdT$$

$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$

$$\left(\frac{\partial \Delta G}{\partial T}\right)_p = -\Delta S \qquad (7.45)$$

Also, $\Delta G = \Delta H - T\Delta S$

Substituting value of ΔS from Eq. (7.45), we get

$$\Delta G = \Delta H + T\left(\frac{\partial \Delta G}{\partial T}\right)_p \tag{7.46}$$

Equation 7.46 is called **Gibb's Helmholtz equation**.

Mathematical proof that maximum non-pV work = decrease in Gibb's free energy:

For any feasible process,

$$\mathrm{d}S_{\text{universe}} \geq 0$$
$$\mathrm{d}S_{\text{system}} + \left(\frac{-q}{T}\right) \geq 0$$
$$\Rightarrow q \leq T\mathrm{d}S_{\text{system}}$$

Therefore,

$$\mathrm{d}U - w_{\text{non-}pV} - w_{pV} \leq T\mathrm{d}S_{\text{system}}$$
$$\mathrm{d}U + p\mathrm{d}V - w_{\text{non-}pV} \leq T\mathrm{d}S_{\text{system}}$$
$$\mathrm{d}(U + pV) - w_{\text{non-}pV} \leq \mathrm{d}(TS)$$

(If T and P are constant.)
Therefore,

$$\mathrm{d}(H - TS)_{T,p} = w_{\text{non-}pV}$$
$$(\mathrm{d}G)_{T,p} \leq w_{\text{non-}pV}$$
$$w_{\text{non-}pV} \leq -(\mathrm{d}G)_{T,p}$$

Chemical Potential of Multicomponent System

In a multicomponent system, change in free energy (dG) at constant temperature and pressure may be expressed in terms of partial molar free energy ($\overline{G}_i$) and number of moles of component n as

$$(\mathrm{d}G)_{T,p} = \sum_i \overline{G}_i \mathrm{d}n_i \quad (i = \text{number of constituents})$$

When temperature and pressure are not constant, free energy change is given by

$$\mathrm{d}G = V\mathrm{d}p - S\mathrm{d}T + \sum_i \overline{G}_i \mathrm{d}n_i$$

The partial molar free energy was also called chemical potential by Gibbs and represented as m, therefore, free energy change is

$$\mathrm{d}G = V\mathrm{d}p - S\mathrm{d}T + \sum_i \mu_i \mathrm{d}n_i$$

When a small amount of substance $i(\mathrm{d}n_i)$ is added to the system, keeping other variables constant, the change in free energy with change in composition is given by

$$(\mathrm{d}G)_{T,p} = \sum_i \mu_i \mathrm{d}n_i \tag{7.47}$$

This is known as **Gibbs–Duhem equation**. It gives the contribution of chemical potential of each component of the mixture per mole to the total free energy of the system at constant temperature and pressure.

The variation of chemical potential of component i of a multicomponent system, as a function of temperature is related to partial molar entropy of the component by the expression

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{p,n_i} = -\overline{S}_i$$

Similarly, the variation of chemical potential of the component *i* of a multicomponent system, as a function of pressure is related to partial molar volume of the component by the expression

$$\left(\frac{\partial \mu_i}{\partial p}\right)_{T,n_i} = -\overline{V}_i$$

van′t Hoff Reaction Isotherm and Equations

Consider the following reaction in equilibrium

$$a\mathrm{A} + b\mathrm{B} \rightleftharpoons c\mathrm{C} + d\mathrm{D}$$

The thermodynamic properties can be expressed in terms of partial molar free energies or chemical potential. For non-ideal system, free energy can be expressed in terms of activity as

$$G = G^{\circ} + RT\ln a$$

Therefore, chemical potential of any component may be expressed in terms of activity as

$$\mu = \mu^{\circ} + RT\ln a$$

In the above system at equilibrium, if the concentration of A and B diminishes by $a\mathrm{d}n$ and $b\mathrm{d}n$ moles, then there is a corresponding increase in concentrations of C and D by $c\mathrm{d}n$ and $d\mathrm{d}n$ moles. The free energy change can be expressed in terms of chemical potential as

$$(\mathrm{d}G)_{T,p} = \Sigma\mu_1\mathrm{d}n_1 = (\mu_{\mathrm{C}}c\mathrm{d}n + \mu_{\mathrm{D}}d\mathrm{d}n) - (\mu_{\mathrm{A}}a\mathrm{d}n + \mu_{\mathrm{B}}b\mathrm{d}n)$$

or $$\Delta G = [c(\mu^{\circ}_{\mathrm{C}} + RT\ln a_{\mathrm{C}}) + d(\mu^{\circ}_{\mathrm{D}} + RT\ln a_{\mathrm{D}}) - (a(\mu^{\circ}_{\mathrm{A}} + RT\ln a_{\mathrm{A}}) + b(\mu^{\circ}_{\mathrm{b}} + RT\ln a_{\mathrm{B}}))]$$

$$\Delta G = [(c\mu^{\circ}_{\mathrm{C}} + d\mu^{\circ}_{\mathrm{D}}) - (a\mu^{\circ}_{\mathrm{A}} + b\mu^{\circ}_{\mathrm{B}})] + RT\ln\left[\frac{a^{c}_{\mathrm{C}}a^{d}_{\mathrm{D}}}{a^{a}_{\mathrm{A}}a^{b}_{\mathrm{B}}}\right]$$

$$0 = \Delta G^{\circ} + RT\ln\left[\frac{a^{c}_{\mathrm{C}}a^{d}_{\mathrm{D}}}{a^{a}_{\mathrm{A}}a^{b}_{\mathrm{B}}}\right] \quad (\text{as } \Delta G = 0 \text{ at equilibrium})$$

or $$-\left(\frac{\Delta G^{\circ}}{RT}\right) = \ln\left[\frac{a^{c}_{\mathrm{C}}a^{d}_{\mathrm{D}}}{a^{a}_{\mathrm{A}}a^{b}_{\mathrm{B}}}\right]$$

therefore, $$\Delta G^{\circ} = -RT\ln K$$

where *K* is called the thermodynamic equilibrium constant and it is the ratio of the activities of products to those of reactants at equilibrium. The free energy change of reaction at any state is given by

$$\Delta G = \Delta G^{\circ} + RT\ln Q = -RT\ln K + RT\ln Q = RT\ln\frac{Q}{K}$$

where *Q* is the reaction quotient and is the ratio of activities of reactants and products at any state of reaction. The relation is known as van′t Hoff reaction isotherm. It is useful for determining the feasibility of a reaction under a given set of conditions. The variation in equilibrium constant *K* with temperature is given by **van′t Hoff equation**

$$\Delta G^{\circ} = -RT\ln K$$

or $$\ln K = -\frac{\Delta G^{\circ}}{RT}$$

Differentiating with respect to T, we get

$$\frac{\partial \ln K}{\partial T} = -\frac{1}{R}\left(\frac{\partial(\Delta G/T)}{\partial T}\right) = -\frac{1}{R}\left(\frac{-\Delta H^\circ}{T^2}\right) \quad \text{(by Gibbs – Helmholtz equation)}$$

$$= \frac{\Delta H}{RT^2} \quad (\text{as } \Delta H \text{ does not vary much with pressure, } \Delta H^\circ = \Delta H)$$

This equation is known as van't Hoff equation. Integrating this equation, we get

$$\ln k = \frac{-\Delta H}{RT} + \text{Constant}$$

or

$$\log k = \frac{-\Delta H}{2.303RT} + \text{Constant}$$

If integration is carried out between the temperatures T_1 and T_2, we get another useful form of van't Hoff equation

$$\log\left(\frac{k_2}{k_1}\right) = \frac{-\Delta H}{2.303R}\left(\frac{T_2 - T_1}{T_1T_2}\right) \tag{7.48}$$

Similarly at constant pressure

$$\frac{\partial \ln K}{\partial T} = \frac{\Delta E}{RT^2}$$

This relation is called **van't Hoff isochore**.

Solved Example 7-56

The standard Gibbs energy change for a reaction is $\Delta G^\circ = -41.8$ kJ mol^{-1} at 700 K and 1 atm. Calculate the equilibrium constant of the reaction at 700 K.

Solution

The standard Gibbs energy and equilibrium constant are related by the equation:

$$\Delta G^\circ = -RT \ln K = -2.303\, RT \log K$$

Given that $\Delta G^\circ = -41.8$ kJ $= -41800$ J, $T = 700$ K and $R = 8.314$ J K^{-1} mol^{-1}. Substituting these values in the equation, we get

$$-41800 = -2.303 \times 8.314 \times 700 \log K$$

$$-41800 = -13403 \log K$$

or

$$\log K = \frac{41800}{13403} = 3.1187 \Rightarrow K = 1.312 \times 10^4$$

Solved Example 7-57

Calculate the equilibrium constant for a reaction at 400 K given that $\Delta H^\circ = 268.3$ kJ mol^{-1} and $\Delta S = 0.857$ kJ K^{-1} mol^{-1} at 400 K.

Solution

The equilibrium constant is related to standard free energy change by the reaction

$$\Delta G^\circ = -RT \ln K = -2.303RT \log K$$

and free energy can be obtained from the relation

$$\Delta G^\circ = \Delta H^\circ - T\Delta S$$

Given that $\Delta H^\circ = 268.3$ kJ mol^{-1}; $\Delta S = 0.857$ kJ K^{-1}; $T = 400$ K. Substituting values, we get

$$\Delta G^\circ = 268.3 - 400 \times 0.857 = -74.5 \text{ kJ} = -74500 \text{ J}$$

Substituting value of ΔG° in the above equation, we get

$$-74500 = -2.303 \times 8.314 \times 400 \times \log K$$

$$\log K = \frac{74500}{7658.8} = 0.9727$$

or

$$K = 9376 = 9.376 \times 10^3$$

Solved Example 7-58

A reaction that can convert coal to methane (the chief component of natural gas) is

$$C(s) + 2H_2(g) \rightleftharpoons CH_4(g)$$

for which $\Delta G^\circ = -50.79$ kJ mol^{-1}. What is the value of K_p for this reaction at 25°C? Does this value of K_P suggest that studying this reaction as a means of methane production is worthwhile pursuing?

Solution

We know that $\Delta G^\circ = -RT \ln K_p$. Substituting the values, we get

$$-50.79 \times 10^3 \text{ J} = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K}) \times \ln K_p$$

or $$\ln K_p = 20.50$$

Taking the exponential of both sides of this equation gives: $K_p = 8.000 \times 10^8$. This is a favorable reaction, since the equilibrium lies far to the side favoring products and is worth studying as a method for methane production.

Solved Example 7-59

The reaction $NO_2(g) + NO(g) \rightleftharpoons N_2O(g) + O_2(g)$ has $\Delta G^\circ_{1273\text{ K}} = -9.67$ kJ. A 1.00 L reaction vessel at 1000°C contains 0.0200 mol NO_2, 0.040 mol NO, 0.015 mol N_2O, and 0.0350 mol O_2. Is the reaction at equilibrium? If not, in which direction will the reaction proceed to reach equilibrium.

Solution

For the reactions in gaseous state, $\Delta G^\circ = -RT \ln K_p$. Substituting values, we get

$$-9.67 \times 10^3 \text{ J} = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(1273 \text{ K}) \times \ln K_p$$

$$\ln K_p = 0.914 \Rightarrow K_p = 2.49$$

Now, $$Q = \frac{[N_2O][O_2]}{[NO_2][NO]} = \frac{(0.015)(0.0350)}{(0.0200)(0.040)} = 0.66$$

Since the value of Q is less than the value of K, the system is not at equilibrium and must shift to the right to reach equilibrium.

7.21 | THIRD LAW OF THERMODYNAMICS

This concept of entropy as a measure of orderliness or randomness, has led to the conclusion that *all substances in their normal crystalline state at the absolute zero temperature would be in the condition of maximum orderly arrangement because all motion has essentially ceased at 0 K*. In other words, entropy of a substance at 0 K is minimum. This observation has led to formulation of the third law of thermodynamics.

The third law was further defined by Lewis and Randall in 1923 as *every substance, element or compound has a finite entropy but at absolute zero of temperature, the entropy may become zero and does become so in the case of a perfectly crystalline substance*.

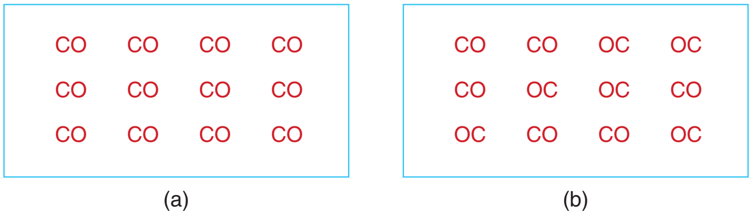
The third law of thermodynamics permits calculations of absolute values of entropy of a pure substance at any temperature. Because we know the point at which entropy has a value of zero, it is possible by *experimental measurement* and calculation to determine the total amount of entropy that a substance has at temperatures above 0 K. If the entropy of one mole of a substance is determined at a temperature of 298 K (25°C) and a pressure of 1 atm, we call it the **standard entropy**, S°.

Once we have the entropies of a variety of substances, we can calculate the **standard entropy change**, ΔS°, for chemical reactions in much the same way as we calculated ΔH° for a reaction.

$$\Delta S^\circ = \Sigma S^\circ(\text{products}) - \Sigma S^\circ(\text{reactants})$$

There are certain substances that possess entropy even when they are cooled close to absolute zero and this entropy is known as **residual entropy**. It is generally exhibited by substances that can exist in different microscopic states even when cooled to 0 K. These substances can exist in different ground states which have only slightly different energies.

To understand the origin of residual entropy, let us consider a molecule of the type AB, where A and B are similar atoms. The energy difference between the arrangement . . . AB AB AB . . . and . . . AB BA AB BA . . . is very small, so the molecules adopt different orientations in the solid crystal, leading to some disorder, and hence, residual entropy. A common example of molecules with residual entropy is carbon monoxide, which has a very small dipole moment. When the crystal is cooled to absolute zero, a few molecules of carbon monoxide align themselves in a manner that they are oriented in the same direction to yield a perfect crystal, while others have random structure which accounts for the residual entropy of 5 J $K^{-1}mol^{-1}$. The molecular arrangement of carbon monoxide molecules in the perfect and actual crystal can be represented as shown in Fig. 7.30.


CO CO CO CO
CO CO CO CO
CO CO CO CO

(a)

CO CO OC OC
CO OC OC CO
OC CO CO OC

(b)

Figure 7.30 Arrangement of CO molecules: (a) Perfect crystal and (b) actual crystal.

> **Note:** Ice was the first material that was proposed to have residual entropy. In a large number of molecules, the hydrogen atoms bonded to each oxygen atom retain some degree of freedom of stretching movement and cause residual entropy. Amorphous glass is another material with residual entropy.

For example, let us find ΔS_{total} for the following reaction

$$\underset{(0\text{ K},\, p\text{ atm})}{\text{A(s)}} \xrightarrow{\Delta S_{\text{total}}} \underset{(T\text{ K},\, p\text{ atm})}{\text{A(g)}}$$

$$\Delta S_{\text{total}} = S_{T,p} - S_{0,p}$$

The above reaction can be written as

$$\begin{tikzcd}
\begin{array}{c}\text{A}(s)\\(0\text{ K}, p\text{ atm})\end{array} \arrow[r, "\Delta S_{\text{total}}"] \arrow[d, "\Delta S_1"'] & \begin{array}{c}\text{A}(g)\\(T\text{K}, p\text{ atm})\end{array} & \begin{array}{c}\text{A}\ (T_{\text{bp}}, p\text{ atm})\\(g)\end{array} \arrow[l, "\Delta S_5"'] \\
\begin{array}{c}\text{A}(s)\\(T_{\text{mp}}, p\text{ atm})\end{array} \arrow[r, "\Delta S_2"] & \begin{array}{c}\text{A(l)}\\T_{\text{mp}}, p\text{ atm}\end{array} \arrow[r, "\Delta S_3"] & \begin{array}{c}\text{A(l)}\\T_{\text{bp}}, p\text{ atm}\end{array} \arrow[u, "\Delta S_4"']
\end{tikzcd}$$

The changes can be depicted as shown in Fig. 7.31. Then,

$$\Delta S_{\text{total}} = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 + \Delta S_5$$

$$S_{T,p} = S_{0,p} + \int_0^{T_{\text{mp}}} \frac{n(C_p)_{\text{solid}}\,dT}{T} + \frac{\Delta H_{\text{fusion}}}{T_{\text{mp}}} + \int_{T_{\text{mp}}}^{T_{\text{bp}}} \frac{n(C_p)_{\text{liquid}}\,dT}{T} + \frac{\Delta H_{\text{vaporization}}}{T_{\text{bp}}} + \int_{T_{\text{bp}}}^{T} \frac{n(C_p)_{\text{gas}}\,dT}{T}$$

Here, $S_{0,p} = 0$ because of the third law of thermodynamics

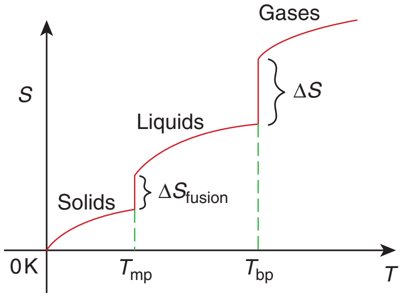


Figure 7.31 Graphical representation for the reaction A(s) ° A(g).

> **Note:**
> 1. $\Delta S_{\text{vaporization}} > \Delta S_{\text{fusion}}$
> 2. Generally slope decreases with increase in temperature for solids because randomness increases manifold at lower temperatures.

T–S Curves for Different Processes

1. **For isothermal process:** Change in entropy is given by

$$dS = \frac{q}{T}$$

For an isothermal process, T is constant, therefore, $q = T dS$

For example, consider the isothermal expansion from state A ° B and compression from B ° A. Then the temperature – entropy (*T–S*) curve is as shown in Fig. 7.32.

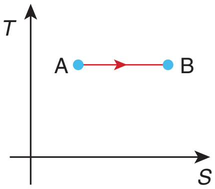


Figure 7.32 *T–S* curve for an isothermal process.

2. **For adiabatic process:** Here, $dS = 0$. So the *T–S* curve for adiabatic compression from state A ° B and expansion from B ° A is as shown in Fig. 7.33.

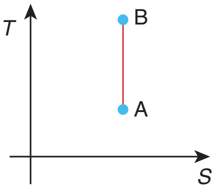


Figure 7.33 *T–S* curve for an adiabatic process.

3. **For Carnot cycle:** Consider the Carnot cycle from state A ° B ° C ° D. The *T–S* curves for various processes are as shown in Fig. 7.34.
   A ° B: Isothermal expansion
   B ° C: Adiabatic expansion
   C ° D: Isothermal compression
   D ° A: Adiabatic compression

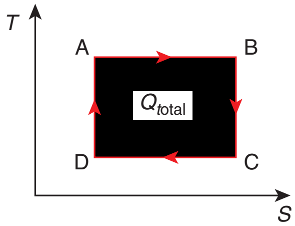


Figure 7.34 *T–S* curve for Carnot cycle.

4. **Isobaric process:** For an isobaric process

$$dS = C_p \frac{dT}{T}$$

Therefore $T = T_0 e^{S/C_p}$

5. **Isochoric process:** For an isochoric process

$$dS = C_V \frac{dT}{T}$$

$$T = T_0 e^{S/C_V}$$

The *T–S* curves for an isobaric and isochoric processes are as shown Fig. 7.35.

Slope of an isochoric process is

$$\frac{dT}{dS} = \frac{T}{C_V}$$

Slope of isobaric process

$$\frac{dT}{dS} = \frac{T}{C_p}$$

Since, $C_p > C_V$, therefore, slope of isochoric process is greater in *T–S* curve.

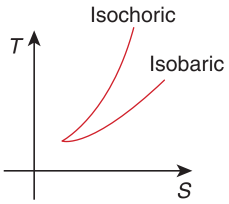


Figure 7.35 *T–S* curves for isobaric and isochoric processes.

SOLVED OBJECTIVE QUESTIONS FROM PREVIOUS YEAR PAPERS

1. For which one of the following equations is $\Delta_r H^\circ$ equal to $\Delta_f H^\circ$?
   (A) $CH_4(g) + 2Cl_2(g) \rightarrow CH_2Cl_2(l) + 2HCl(g)$
   (B) $Xe(g) + 2F_2(g) \rightarrow XeF_4(g)$
   (C) $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$
   (D) $N_2(g) + O_3(g) \rightleftharpoons N_2O_3(g)$ **(IIT-JEE 2003)**

Solution

(B) For this reaction, $\Delta_r H^\circ = \Delta_f H^\circ$.

2. Spontaneous adsorption of a gas on solid surface is an exothermic process because
   (A) ΔH increases for system.
   (B) ΔS increases for gas
   (C) ΔS decreases for gas.
   (D) ΔG increases for gas. **(IIT-JEE 2004)**

Solution

(C) For a spontaneous process, ΔG should be negative. Also, the process is exothermic (means ΔH is also negative).

For adsorption of gas to be spontaneous, the entropy should decrease in accordance with the relation $\Delta G = \Delta H - T\Delta S$.

3. 2 mol of an ideal gas expanded isothermally and reversibly from 1 L to 10 L at 300 K. What is the enthalpy change?
(A) 4.98 kJ (B) 11.47 kJ
(C) –11.47 kJ (D) 0 kJ **(IIT-JEE 2004)**

Solution

(D) $H = U + pV$ or $\Delta H = \Delta U + \Delta(pV)$.
Now, $\Delta H = \Delta U + nR\Delta T$
For isothermal and reversible expansion $\Delta U = 0$ and $\Delta T = 0$.
So, $\Delta H = 0 + 0 = 0$

4. $\Delta H_{\text{vap}} = 30$ kJ mol^{-1} and $\Delta S_{\text{vap}} = 75$ J mol^{-1} K^{-1}. Find the temperature of vapor at 1 atm. **(IIT-JEE 2004)**
(A) 400 K (B) 350 K
(C) 298 K (D) 250 K

Solution

(A) $\Delta G = \Delta H - T\Delta S$. At equilibrium $\Delta G = 0$. So,

$$T = \frac{\Delta H}{\Delta S} = \frac{30 \times 10^3}{75} = 400\,\text{K}$$

5. One mole of a monatomic ideal gas expands adiabatically at initial temperature T against a constant external pressure of 1 atm from 1 L to 3 L. The final temperature of the gas is
(A) T (B) $T/3^{(5R/2)}$
(C) $T - 2/(1.5 \times 0.082)$ (D) $T + 2/(1.5 \times 0.082)$
(IIT-JEE 2005)

Solution

(C) Work done against constant pressure $p = p_{\text{ext}}(V_1 - V_2)$

In adiabatic condition, $\Delta q = 0$ and $w = \Delta U$.

Therefore, $-p_{\text{ext}}(V_1 - V_2) = \frac{3}{2}R(T_1 - T_2)$

(Since the expansion work is negative.)

$$-p_{\text{ext}}(V_1 - V_2) = \frac{3}{2}RT_2 - \frac{3}{2}RT_1$$

Given that $p_{\text{ext}} = 1$ atm, $V_2 = 3$ L and $V_1 = 1$ L. Substituting and solving, we get

$$T_2 = T_1 - \frac{2}{(3/2)R} = T_1 - \frac{2}{1.5 \times 0.0821}$$

6. The direct conversion of A to B is difficult; hence it is carried out by the following path shown in Fig. 7.36.

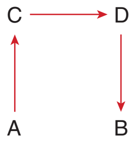


Figure 7.36

Given that

$$\Delta S_{(A\to C)} = 50\,\text{eu},\ \Delta S_{(C\to D)} = 30\ \text{eu},\ \Delta S_{(B\to D)} = 20\,\text{eu}$$

where eu is entropy unit. Then $\Delta S_{(A\to B)}$ is
(A) +100 eu (B) +60 eu
(C) –100 eu (D) –60 eu **(IIT-JEE 2006)**

Solution

(B) $\Delta S_{A\to B} = \Delta S_{A\to C} + \Delta S_{(C\to D)} - \Delta S_{B\to D}$
$= 50 + 30 - 20 = +60\,\text{eu}$

7. The value of $\log_{10}K$ for a reaction $A \to B$ is
(Given: $\Delta_r H_{298\,K} = -54.07$ kJ mol^{-1} and
$R = 8.314$ JK^{-1}mol^{-1}; $2.303 \times 8.314 \times 298 = 5705$.)
(A) 5 (B) 10
(C) 95 (D) 100 **(IIT-JEE 2007)**

Solution

(B) $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -54.07 - 298 \times 10$
$= -54070 - 2980 = -57050$ J mol^{-1}

Note that $\Delta G^\circ = -2.303RT\log K$. Substituting values, we get

$$\log K = \frac{57050}{2.303 \times 8.314 \times 298} = \frac{57050}{5705} = 10$$

8. For the process $H_2O(l, 1\,\text{bar}, 373\,\text{K}) \rightarrow H_2O(g, 1\,\text{bar}, 373\,\text{K})$, the correct set of thermodynamic parameters is
(A) $\Delta G = 0, \Delta S = +\text{ve}$ (B) $\Delta G = 0, \Delta S = -\text{ve}$
(C) $\Delta G = +\text{ve},\ \Delta S = 0$ (D) $\Delta G = -\text{ve}, \Delta S = +\text{ve}$
(IIT-JEE 2007)

Solution

(A) At 100°C, H_2O in liquid state has equilibrium with H_2O in vapor phase; therefore, $\Delta G = 0$. Also, the liquid molecules are converting into gaseous phase and we know that the randomness of system increases from the liquid to gaseous phase, so, ΔS = positive.

9. **Statement 1:** For every chemical reaction at equilibrium, standard Gibbs energy of reaction is zero.
Statement 2: At constant temperature and pressure, chemical reactions are spontaneous in the direction of decreasing Gibbs energy.
(A) Statement 1 is True, Statement 2 is True: Statement 2 is a correct explanation for Statement 1.
(B) Statement 1 is True, Statement 2 is True; Statement 2 is NOT a correct explanation for Statement 1.
(C) Statement 1 is True, Statement 2 is False.
(D) Statement 1 is False, Statement 2 is True.
(IIT-JEE 2008)

Solution

(D) At equilibrium $\Delta G = 0$, ΔG° of a reaction may or may not be zero. For a spontaneous reaction, $\Delta G < 0$.

10. **Statement 1:** There is a natural asymmetry between converting work to heat and converting heat to work.

Statement 2: No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work.

(A) Statement 1 is True, Statement 2 is True; Statement 2 is a correct explanation for Statement 1.
(B) Statement 1 is True, Statement 2 is True; Reason is NOT a correct explanation for Statement 1.
(C) Statement 1 is True, Statement 2 is False.
(D) Statement 1 is False, Statement 2 is True. **(IIT-JEE 2008)**

Solution

(A) Conceptual, based on second law of thermodynamics.

11. In a constant-volume calorimeter, 3.5 g of a gas with molar mass 28 g mol^{-1} was burnt in excess oxygen at 298.0 K. The temperature of the calorimeter was found to increase from 298.0 K to 298.45 K due to the combustion process. Given that the heat capacity of the calorimeter is 2.5 kJ K^{-1}, the numerical value for the change in internal energy of combustion of the gas in kJ mol^{-1} is __________. **(IIT-JEE 2009)**

Solution

(9) Energy released at constant volume due to combustion of 3.5 g of a gas $= 2.5 \times 0.45$. Hence, energy released due to combustion of 28 g (i.e., 1 mol) of a gas $= (2.5 \times 0.45 \times 28)/3.5 = 9$ kJ mol^{-1}.

12. Among the following, the state function(s) is (are)
(A) internal energy.
(B) irreversible expansion work.
(C) reversible expansion work.
(D) molar enthalpy. **(IIT-JEE 2009)**

Solution

(A), (D) Both internal energy and molar enthalpy depend only on the initial and final states, not on the path followed.

13. The species which by definition has zero standard molar enthalpy of formation at 298 K is
(A) $Br_2(g)$ (B) $Cl_2(g)$
(C) $H_2O(g)$ (D) $CH_4(g)$ **(IIT-JEE 2010)**

Solution

(B) Cl_2 is a gas at 298 K while Br_2 is a liquid.

14. Among the following, the intensive property is (properties are)
(A) molar conductivity. (B) electromotive force.
(C) resistance. (D) heat capacity.
(IIT-JEE 2010)

Solution

(A), (B) Resistance and heat capacity are mass-dependent properties, hence extensive.

15. One mole of an ideal gas is taken from **a** to **b** along two paths denoted by the solid and the dashed lines as shown in the graph (Fig. 7.37). If the work done along the solid line path is w_s and that dotted line path is w_d, then the integer closest to the ratio w_d/w_s is __________. **(IIT-JEE 2010)**

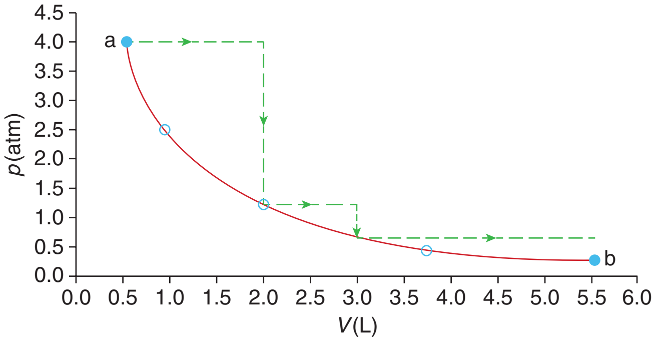


Figure 7.37

Solution

(2) The work done along the dotted line w_d is calculated as

$$\begin{aligned} w_d &= 4 \times 1.5 + 1 \times 1 + 0.75 \times 2.5 \\ &= 8.667 \text{ L atm} \end{aligned}$$

The process depicted by the solid line is isothermal.

$$\begin{aligned} w_s &= -2 \times 2.303 \log \frac{5.5}{0.5} = -2 \times 2.303 \times \log 11 \\ &= -2 \times 2.303 \times 1.0414 = -4.79 \end{aligned}$$

$$\frac{w_d}{w_s} = \frac{8.65}{4.79} = 1.80 = 2$$

15. Match the transformations in Column I with appropriate options in Column II

Column I	Column II
(A) $CO_2(s) \to CO_2(g)$	(p) Phase transition
(B) $CaCO_3(s) \to CaO(s) + CO_2(g)$	(q) Allotropic change
(C) $2H(g) \to H_2(g)$	(r) ΔH is positive
(D) P(white, solid) $\to$ P(red, solid)	(s) ΔS is positive
	(t) ΔS is negative

(IIT-JEE 2011)

Solution

A → (p, r, s); B → r, s; C → (t); D → (q, r, t)

(A) $CO_2(s) \to CO_2(g)$ $\Delta H = +\text{ve}$, phase transition and $\Delta S = +\text{ve}$.
(B) $CaCO_3(s) \to CaO(s) + CO_2(g)$ $\Delta H = +\text{ve}$, no phase transition and $\Delta S = +\text{ve}$.
(C) $2H(g) \to H_2(g)$. Two particles give one gaseous particle, so $\Delta S = -\text{ve}$.
(D) P(white, solid) $\to$ P(red, solid) $\Delta H = +\text{ve}$, $\Delta S = +\text{ve}$, allotropic change, that is, phosphorus is getting changed from one allotrope form into another.

16. For an ideal gas, consider only p–V work in going from an initial state X to the final state Z. The final state Z can be reached by either of the two paths shown in the Fig. 7.38. Which of the following choice(s) is(are) correct? [Take ΔS as change in entropy and w as work done]

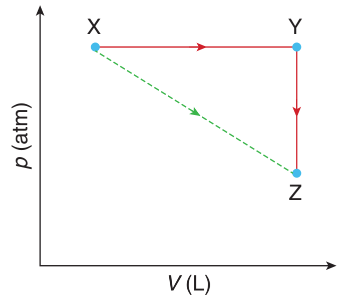


Figure 7.38

(IIT-JEE 2012)

(A) $\Delta S_{X\to Z} = \Delta S_{X\to Y} + \Delta S_{Y\to Z}$

(B) $w_{X\to Z} = w_{X\to Y} + w_{Y\to Z}$

(C) $w_{X\to Y\to Z} = w_{X\to Y}$

(D) $\Delta S_{X\to Y\to Z} = \Delta S_{X\to Y}$

Solution

(A, C) As entropy is a state function and is additive

$$\Delta S_{X\to Z} = \Delta S_{X\to Y} + \Delta S_{Y\to Z}$$

On moving from Y to Z, the work done is zero as the volume is kept constant (isochoric process)

$$w_{X\to Y\to Z} = w_{X\to Y}$$

17. The reversible expansion of an ideal gas under adiabatic and isothermal conditions is shown in Fig. 7.39. Which of the following statement(s) is (are) correct?

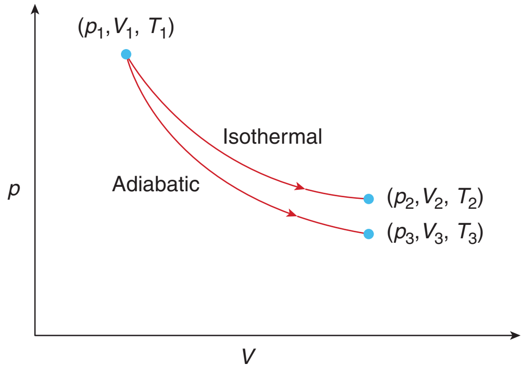


Figure 7.39

(A) $T_1 = T_2$ (B) $T_3 > T_1$

(C) $w_{\text{isothermal}} > w_{\text{adiabatic}}$ (D) $\Delta U_{\text{isothermal}} > \Delta U_{\text{adiabatic}}$

(IIT-JEE 2012)

Solution

(A, D) For isothermal process, $T_1 = T_2$. Work done in isothermal process is less than adiabatic process. In case of isothermal process, the temperature remains constant so there is no change in the internal energy, whereas in case of adiabatic process expansion occurs through internal energy.

19. The standard enthalpies of formation of CO_2 (g), H_2O (l) and glucose(s) at 25°C are –400 kJ mol^{-1}, –300 kJ mol^{-1} and –1300 kJ mol^{-1}, respectively. The standard enthalpy of combustion per gram of glucose at 25°C is

(A) +2900 kJ (B) –2900 kJ

(C) –16.11 kJ (D) +16.11 kJ

(JEE Advanced 2013)

Solution

(C) The reaction involved is

$$C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$$

$$\Delta H = \Sigma\Delta H(\text{products}) - \Sigma\Delta H(\text{reactants})$$

$$= 6(-400) + 6(-300) - (-1300) = -2900 \text{ kJ mol}^{-1}$$

Now, 1 mol of glucose = 180 g of glucose, so enthalpy of combustion per gram of glucose at 25°C is

$$\Delta H = \frac{-2900}{180} = -16.11 \text{ kJ g}^{-1}$$

20. Benzene and naphthalene form an ideal solution at room temperature. For this process, the true statement(s) is(are)

(A) ΔG is positive. (B) ΔS_{system} is positive

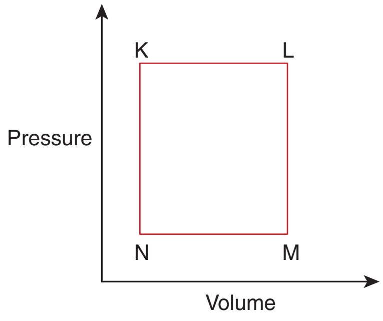
(C) $\Delta S_{\text{surroundings}} = 0$ (D) $\Delta H = 0$

(JEE Advanced 2013)

Solution

(B), (C), (D) For an ideal solution formed by benzene and naphthalene, $\Delta H_{\text{mixing}} = 0$, $\Delta S_{\text{system}} > 0$ and $\Delta S_{\text{surroundings}} = 0$.

Paragraph for Questions 21 and 22: A fixed mass m of a gas is subjected to transformation of states from K to L to M to N and back to K as shown in the figure



21. The succeeding operations that enable this transformation of states are

(A) Heating, cooling, heating, cooling

(B) Cooling, heating, cooling, heating

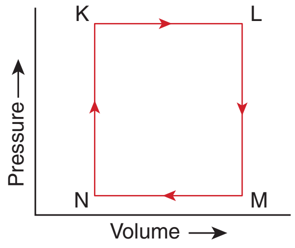
(C) Heating, cooling, cooling, heating

(D) Cooling, heating, heating, cooling

(JEE Advanced 2013)

Solution

(C) From the graph



As the term pV increases, the temperature increases; and when pV decreases the temperature decreases.

The term pV increases K ° L, so this involves heating and is an isobaric process.

It increases from N ° K, so this involves heating and is an isochoric process.

It decreases from M ° N, so this involves cooling and is an isobaric process.

It decreases from L ° M, so this involves cooling and is an isochoric process.

22. The pair of isochoric processes among the transformation of states is

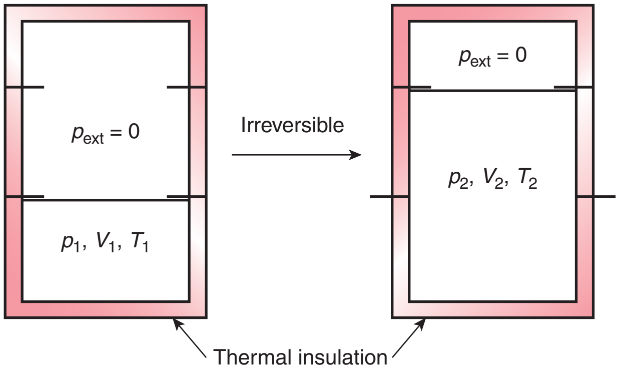
(A) K to L and L to M
(B) L to M and N to K
(C) L to M and M to N
(D) M to N and N to K

(JEE Advanced 2013)

Solution

(B) From the above solution, we have
From K ° L: heating (isobaric)
From L ° M: cooling (isochoric)
From M ° N: cooling (isobaric)
From N ° K: heating (isochoric)

23. An ideal gas in a thermally insulated vessel at internal pressure = p_1, volume = V_1 and absolute temperature = T_1 expands irreversibly against zero external pressure, as shown in the diagram. The final internal pressure, volume and absolute temperature of the gas are p_2, V_2 and T_2, respectively. For this expansion,



(A) $q = 0$
(B) $T_2 = T_1$
(C) $p_2V_2 = p_1V_1$
(D) $p_2V_2^\gamma = p_1V_1^\gamma$

(JEE Advance 2014)

Solution

(A), (B), (C) As the vessel is thermally insulated so, $q = 0$. Therefore, $\Delta U = 0$, $\Delta T = 0 \Rightarrow T_1 = T_2$. According to combined gas law equation,

$$\frac{p_2V_2}{T_2} = \frac{p_1V_1}{T_1} \Rightarrow p_2V_2 = p_1V_1$$

24. For the process

$$H_2O(l) \;°\; H_2O(g)$$

at $T = 100$°C and 1 atmosphere pressure, the correct choice is

(A) $\Delta S_{system} > 0$ and $\Delta S_{surroundings} > 0$
(B) $\Delta S_{system} > 0$ and $\Delta S_{surroundings} < 0$
(C) $\Delta S_{system} < 0$ and $\Delta S_{surroundings} > 0$
(D) $\Delta S_{system} < 0$ and $\Delta S_{surroundings} < 0$

(JEE Advanced 2014)

Solution

(B) We know that

$\Delta S_{system} + \Delta S_{surroundings} = 0 \Rightarrow \Delta S_{system} = -\Delta S_{surroundings}$

For the given reaction, $\Delta S_{system} > 0$ and therefore, $\Delta S_{surroundings} < 0$.

25. Match the thermodynamic processes given under column I with the expressions given in Column II

Column I	Column II
(A) Freezing of water at 273 K and 1 atm	(p) $q = 0$
(B) Expansion of 1 mol of an ideal gas into a vacuum under isolate conditions	(q) $w = 0$
(C) Mixing of equal volumes of two ideal gases at constant temperature and pressure in an isolated container	(r) $\Delta S_{system} < 0$
(D) Reversible heating of H_2 (g) at 1 atm from 300 K to 600 K, followed by reversible cooling to 300 K at 1 atm	(s) $\Delta U = 0$
	(t) $\Delta G = 0$

(JEE Advanced 2015)

Solution

A ° (r, t); B ° (p, q, s), B ° (p, q, s), D ° (p, q, s, t)

A ° During freezing of water entropy decreases, $\Delta S_{sys} < 0$, $\Delta G = 0$.

B ° In vacuum, free expansion work done = 0. So, $q = 0$ and $\Delta U = 0$.

C ° For an ideal gas in isolated condition $q = 0$, $\Delta U = 0$, so as per first law $w = 0$.

D ° The process is cyclic through unique reversible path, hence $\Delta U = 0$ (cyclic), $\Delta G = 0$.

$w = 0$ (positive and negative work are same and opposite) and $q = 0$.

26. The correct relationship between free energy change in a reaction and the corresponding equilibrium constant K_C is

(A) $\Delta G = RT \ln K_C$
(B) $-\Delta G = RT \ln K_C$
(C) $\Delta G^o = RT \ln K_C$
(D) $-\Delta G^o = RT \ln K_C$

(AIEEE 2003)

Solution

(D) $\Delta G^{o} = -RT \ln K_C$ or $-\Delta G^{o} = RT \ln K_C$.

27. If at 298 K the bond energies of C

Given that the standard states for iodine and chlorine are $I_2(s)$ and $Cl_2(g)$, the standard enthalpy of formation for $ICl(g)$ is

(A) –14.6 kJ mol^{-1} (B) –16.8 kJ mol^{-1}

(C) +16.8 kJ mol^{-1} (D) +244.8 kJ mol^{-1}

(AIEEE 2006)

Solution

(C) The required equation is

$$\tfrac{1}{2}I_2(s)+\tfrac{1}{2}Cl_2(g)\rightarrow ICl(g)$$

$$\Delta H=\left[\frac{1}{2}\Delta H_{I_{2(s)}\rightarrow I_{2(g)}}+\frac{1}{2}\Delta H_{I-I}+\frac{1}{2}\Delta H_{Cl-Cl}\right]-[\Delta H_{I-Cl}]$$

$$=\left[\frac{1}{2}\times 62.76+\frac{1}{2}\times 151.0+\frac{1}{2}\times 242.3\right]-[211.3]$$

$$=228.03-211.3=16.73\ \text{kJ mol}^{-1}$$

37. (ΔH – ΔU) for the formation of carbon monoxide (CO) from its elements at 298 K is ($R = 8.314$ J K^{-1} mol^{-1})

(A) –1238.78 J mol^{-1} (B) 1238.78 J mol^{-1}

(C) –2477.57 J mol^{-1} (D) 2477.57 J mol^{-1}

(AIEEE 2006)

Solution

(A) We know that $H = U + pV$. So,

$$\Delta H = \Delta U + \Delta(pV) \Rightarrow \Delta H - \Delta U = \Delta(pV)$$

Also, $\Delta(pV) = \Delta n_g RT$ for an ideal gas.

Therefore, $\Delta H - \Delta U = \Delta n_g RT$

Now, $\Delta n_g = 2$ for the reaction $O_2(g) + 2C(s) \rightarrow 2CO(g)$. So,

$$\Delta H-\Delta U=-\frac{1}{2}\times 8.314\times 298=-1238.78\ \text{J mol}^{-1}$$

38. In the conversion of limestone to lime, $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$, the values of ΔH° and ΔS° are 179.1 kJ mol^{-1} and 160.2 J K^{-1}, respectively, at 298 K and 1 bar. Assuming that ΔH° and ΔS° do not change with temperature, the temperature above which conversion of limestone to lime is

(A) 11118 K (B) 1008 K

(C) 1200 K (D) 845 K

(AIEEE 2007)

Solution

(A) We will find out the equilibrium temperature at which $\Delta G = 0$. We know that

$$\Delta G = \Delta H - T\Delta S$$

$$0 = \Delta H - T\Delta S$$

Therefore, $\Delta H = T\Delta S$. Hence,

$$T=\frac{179.1\times 1000}{160.2}=1118\,\text{K}$$

39. Assuming that water vapor is an ideal gas, the internal energy change (ΔU) when 1 mol of water is vaporized at 1 bar pressure and 100°C will be (given that molar enthalpy of vaporization of water at 1 bar and 373 K is 41 kJ mol^{-1} K^{-1})

(A) 4.1 kJ mol^{-1} (B) 3.7904 kJ mol^{-1}

(C) 37.904 kJ mol^{-1} (D) 41.0 kJ mol^{-1}

(AIEEE 2007)

Solution

(D) The reaction is

$$H_2O(l)\xrightarrow{\text{Vaporization}}H_2O(g)$$

Where $\Delta n_g = 1 - 0 = 1$. Now,

$$\Delta H = \Delta U + \Delta n_g RT$$

$$\Delta U = \Delta H - \Delta n_g RT = 41–8.3 \times 10^{-3} \times 373$$

$$= 37.9\ \text{kJ mol}^{-1}$$

(AIEEE 2007)

40. Oxidizing power of chlorine in aqueous solution can be determined by the parameters indicated below.

$$\tfrac{1}{2}Cl_2(g)\xrightarrow{\frac{1}{2}\Delta_{diss}H^\circ}Cl(g)\xrightarrow{\Delta_{ion}H^\circ}Cl^-(g)\xrightarrow{\Delta_{hyd}H^\circ}Cl^-(aq)$$

The energy involved in the conversion of $\tfrac{1}{2}Cl_2(g)$ to $Cl^-(g)$ (using the data, $\Delta_{diss}H^\circ_{Cl_2} = 240$ kJ mol^{-1}, $\Delta_{ion}H^o_{Cl} = –349$ kJ mol^{-1}, $\Delta_{hyd}H^o_{Cl} = –381$ kJ mol^{-}) will be

(A) +152 kJ mol^{-1} (B) –610 kJ mol^{-1}

(C) –850 kJ mol^{-1} (D) +120 kJ mol^{-1}

Solution

(B) For the reaction

$$\tfrac{1}{2}Cl_2(g)\rightarrow Cl^-(aq);$$

$$\Delta H=\frac{\Delta H_1}{2}+\Delta H_2+\Delta H_3$$

$$=\frac{240}{2}–349–381=–610\ \text{KJ mol}^{-1}$$

(AIEEE 2008)

41. Standard entropies of X_2, Y_2 and XY_3 are 60, 40 and 50 J $K^{-1}mol^{-1}$, respectively. For the reaction,

$$\tfrac{1}{2}X_2+\tfrac{3}{2}Y_2\rightarrow XY_3$$

(AIEEE 2008)

$\Delta H = –30$ kJ, to be at equilibrium, the temperature will be

(A) 1250 K (B) 500 K

(C) 750 K (D) 1000 K

Solution

(C) $\tfrac{1}{2}X_2+\tfrac{3}{2}Y_2\rightarrow XY_3 \cdot \Delta H = –30$ kJ

$$\Delta_r S=50-\left(\frac{3}{2}\times 40+\frac{1}{2}\times 60\right)=-40\ \text{J mol}^{-1}$$

Since, $\Delta G = \Delta H - T\Delta S$ and at equilibrium $\Delta G = 0$, we have

$$T=\frac{\Delta H}{\Delta S}=\frac{-30}{-40}\times 10^3=750K$$

42. In a fuel cell, methanol is used as fuel and oxygen gas is used as an oxidizer. The reaction is

$$CH_3OH(I)+\tfrac{3}{2}O_2(g)\rightarrow CO_2(g)+2H_2O(I)$$

At 298 K, standard Gibbs energies of formation for $CH_3OH(I)$, $H_2O(I)$ and CO_2 (g) are –166.2, –237.2 and –394.4 kJ mol^{-1}, respectively. If standard enthalpy of combustion of methanol is –726 kJ mol^{-1}, efficiency of the fuel cell will be:

(A) 90% (B) 97%

(C) 80% (C) 87% **(AIEEE 2009)**

Solution

(B)

$$CH_3OH(I) + \tfrac{3}{2}\,O_2(g) \rightarrow CO_2 + 2H_2\,O(I)$$

$$\begin{aligned}\Delta G^\circ &= \Delta G^\circ(CO_2) + 2\Delta G^\circ(H_2O) - \Delta G^\circ(CH_3OH)\\ &= -394 - 2(237.2) + 166.2 = -\,702.6 \text{ kJ mol}^{-1}\end{aligned}$$

$$\text{Efficiency of fuel cell} = \frac{\Delta G^\circ}{\Delta H^\circ} = \frac{-702.6}{-726} \times 100 = 97\%$$

43. On the basis of the following thermochemical data:

$$(\Delta, G^\circ H^+(aq) = 0$$

$H_2O(l) \rightarrow H^+(aq) + OH^-(aq)$; $\Delta H = 57.32$ KJ

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$; $\Delta H = -\,286.20$ KJ

The value of enthalpy of formation of OH^- ion at 25° is:

(A) +228.88 kJ (B) –343.52 kJ
(C) –22.88 kJ (D) –228.88 kJ

(AIEEE 2009)

Solution

(D) Adding the given equations, we ger

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H^+(aq) + OH^-(aq)$$

$$\Delta H = -\,228.88 \text{ KJ mol}^{-1}$$

Now, $\Delta_f H^\circ$ of $H^+(aq) = 0$, so $\Delta_f H^\circ$ of $OH^-(aq) = -228.88$ kJ.

44. The standard enthalpy of formation of NH_3 is –46.0 kJ mol^{-1}. If the enthalpy of formation of H_2 from its atoms is –436 kJ mol^{-1} and that of N_3 is –712 kJ mol^{-1}, the average bond enthalpy of N

REVIEW QUESTIONS

1. Why do standard reference values for temperature and pressure have to be selected when we consider and compare heats of reaction for various reactions? What are the values for the standard temperature and standard pressure?

2. What distinguishes a thermochemical equation from an ordinary chemical equation?

3. Why are fractional coefficients permitted in a balanced thermochemical equation? If a formula in a thermochemical equation has a coefficient of (1/2), what does it signify?

4. What two conditions must be met by a thermochemical equation so that its standard enthalpy change can be given the symbol $\Delta_f H^\circ$?

5. Calculate ΔH° in kilojoules for the following reaction, the preparation of the unstable acid nitrous acid, HNO_2.

$$HCl(g) + NaNO_2(s) \longrightarrow HNO_2(l) + NaCl(s)$$

Use the following thermochemical equations.

$$\begin{array}{ll}
2NaCl(s) + H_2O(l) \rightarrow 2HCl(g) + Na_2O(s) & \Delta H^\circ = +507.31\text{ kJ} \\
NO(g) + NO_2(g) + Na_2O(s) \rightarrow 2NaNO_2(s) & \Delta H^\circ = -427.14\text{ kJ} \\
NO(g) + NO_2(g) \rightarrow N_2O(g) + O_2(g) & \Delta H^\circ = -42.68\text{ kJ} \\
2HNO_2(l) \rightarrow N_2O(g) + O_2(g) + H_2O(l) & \Delta H^\circ = +34.35\text{ kJ}
\end{array}$$

6. Which quantities in the statement of the first law are state functions and which are not?

7. What are the units of $p\Delta V$ if pressure is expressed in pascals and volume is expressed in cubic meters?

8. Which of the following changes is accompanied by the most negative value of ΔU?
- **(a)** A spring is compressed and heated.
- **(b)** A compressed spring expands and is cooled.
- **(c)** A spring is compressed and cooled.
- **(d)** A compressed spring expands and is heated.

9. At constant pressure, what role does the enthalpy change play in determining the spontaneity of an event?

10. How do the probabilities of the initial and final states in a process affect the spontaneity of the process?

11. How is the entropy of a substance affected by
- **(a)** an increase in temperature,
- **(b)** a decrease in volume,
- **(c)** changing from a liquid to a solid, and
- **(d)** dissociating into individual atoms?

12. An instant cold pack contains a packet of solid ammonium nitrate surrounded by a pouch of water. When the packet of NH_4NO_3 is broken, the solid dissolves in water and a cooling of the mixture occurs because the solution process for NH_4NO_3 in water is endothermic. Explain, in terms of what happens to the molecules and ions, why this mixing occurs spontaneously.

13. Would you expect the entropy of an alloy (a solution of two metals) to be zero at 0 K? Explain your answer.

14. When glucose is oxidized by the body to generate energy, part of the energy is used to make molecules of ATP (adenosine triphosphate). However, of the total energy released in the oxidation of glucose, only 38% actually goes to making ATP. What happens to the rest of the energy?

15. When a warm object is placed in contact with a cold one, they both gradually come to the same temperature. On a molecular level, explain how this is related to entropy and spontaneity.

16. Considering the fact that the formation of a bond between two atoms is exothermic and is accompanied by an entropy decrease, explain why all chemical compounds decompose into individual atoms if heated to a high enough temperature.

17. Why are the heats of formation of gaseous atoms from their elements endothermic quantities?

18. Show that for an isothermal expansion of an ideal gas,
- **(a)** $\Delta V = 0$ and
- **(b)** $\Delta H = 0$

19. Many reactions that have large negative values of ΔG° are not actually observed to happen at 25°C and 1 atm. Why?

20. What factors must you consider to determine the sign of ΔS for the reaction $2HI(g) \rightarrow H_2(g) + I_2(s)$?

21. Predict the algebraic sign of the entropy change for the following reactions.
- **(a)** $I_2(s) \rightarrow I_2(g)$
- **(b)** $Br_2(g) + 3Cl_2(g) \rightarrow 2BrCl_3(g)$
- **(c)** $NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$
- **(d)** $CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(s)$

22. Approximately how much energy would be released during the formation of the bonds in one mole of acetone molecules?

26. When potassium iodide dissolves in water, the mixture becomes cool. For this change, which is of a larger magnitude, $T\Delta S$ or ΔH?

27. The enthalpy of combustion, $\Delta_c H°$ of oxalic acid, $H_2C_2O_4(s)$, is –246.05 kJ mol^{-1}. Consider the following data:

Substance	$\Delta_f H°$ (kJ mol^{-1})	S° (J mol^{-1} K^{-1})
$C(s)$	0	5.69
$CO_2(g)$	–393.5	213.6
$H_2(g)$	0	130.6
$H_2O(l)$	–285.8	69.96
$O_2(g)$	0	205.0
$H_2C_2O_4(s)$	?	120.1

(a) Write the balanced thermochemical equation that describes the combustion of one mole of oxalic acid.

(b) Write the balanced thermochemical equation that describes the formation of one mole of oxalic acid.

(c) Use the information in the table above and the equations in parts (a) and (b) to calculate ΔH_f° for oxalic acid.

(d) Calculate $\Delta_f S°$ for oxalic acid and $\Delta S°$ for the combustion of one mole of oxalic acid.

(e) Calculate $\Delta_f G°$ for oxalic acid and $\Delta G°$ for the combustion of one mole of oxalic acid.

NUMERICAL PROBLEMS

1. A 5.00 g mass of a metal was heated to 100.0°C and then plunged into 100.0 g of water at 24.0°C. The temperature of the resulting mixture became 28.0°C.

(a) How many joules did the water absorb?
(b) How many joules did the metal lose?
(c) What is the heat capacity of the metal sample?
(d) What is the specific heat of the metal?

2. A sample of copper was heated to 120°C and then thrust into 200 g of water at 25.00°C. The temperature of the mixture became 26.5°C.

(a) How much heat in joules was absorbed by the water?
(b) The copper sample lost how many joules?
(c) What was the mass in grams of the copper sample?

3. What is the molar heat capacity of ethyl alcohol, C_2H_5OH, in units of J mol^{-1}°C^{-1}, if its specific heat is 0.586 cal g^{-1}°C^{-1}?

4. A dilute solution of hydrochloric acid with a mass of 610.29 g and containing 0.33183 mol of HCl was exactly neutralized in a calorimeter by the sodium hydroxide in 615.31 g of a dilute NaOH solution. The temperature increased from 16.784 to 20.610°C. The specific heat of the HCl solution was 4.031 J g^{-1}°C^{-1}; that of the NaOH solution was 4.046 J g^{-1}°C^{-1}. The heat capacity of the calorimeter was 77.99 J°C^{-1}. Write the balanced equation for the reaction. Use the data above to calculate the heat evolved. What is the heat of neutralization per mole of HCl? Assume that the original solutions made independent contributions to the total heat capacity of the system following their mixing.

5. A 1.5 g sample of liquid toluene was placed in a bomb calorimeter along with excess oxygen. When the combustion of the toluene was initiated, the temperature of the calorimeter rose from 25.000°C to 26.413°C. The products of the combustion are $CO_2(g)$ and $H_2O(l)$, and the heat capacity of the calorimeter was 45.06 kJ°C^{-1}.

(a) Write the balanced chemical equation for the reaction in the calorimeter.
(b) How many joules were liberated by the reaction?
(c) How many joules would be liberated under similar conditions if 1.00 mol of toluene were burned?

6. Ammonia reacts with oxygen as follows.

(a) Calculate the enthalpy change for the combustion of 1 mol of NH_3.
(b) Write the thermochemical equation for the reaction in which one mole of H_2O is formed.

$$4NH_3(g) + 7O_2(g) \rightarrow 4NO_2(g) + 6H_2O(g);$$
$$\Delta H° = -1132 \text{ kJ}$$

7. Construct an enthalpy diagram for the formation of $NO_2(g)$ from its elements by two pathways: first, from its elements and, second, by a two-step process, also from the elements. The relevant thermochemical equations are

$$\tfrac{1}{2}N_2(g) + O_2(g) \rightarrow NO_2(g) \qquad \Delta H° = +33.8 \text{ KJ}$$
$$\tfrac{1}{2}N_2(g) + \tfrac{1}{2}O_2(g) \rightarrow NO(g) \qquad \Delta H° = +90.37 \text{ KJ}$$
$$NO(g) + \tfrac{1}{2}O(g) \rightarrow NO_2(g) \qquad \Delta H° = ?$$

Be sure to note the signs of the values of $\Delta H°$ associated with arrows pointing up or down. Using the diagram, determine the value of $\Delta H°$ for the third equation.

8. A 2 kg piece of granite with a specific heat of 0.803 J g^{-1} C^{-1} and a temperature of 95°C is placed into 2 L of water at 22.0°C. When the granite and water come to the same temperature, what will that temperature be?

9. Suppose a truck with a mass of 14 tons (1 ton = 907.18 kg) is traveling at a speed of 72.42 km h^{-1}. If the truck driver slams on the brakes, the kinetic energy of the truck is changed to heat as the brakes slow the truck to a stop. How much would the temperature of 19 L of water increase if all the heat could be absorbed by the water?

10. Ethanol, C_2H_5OH, is made industrially by the reaction of water with ethylene, C_2H_4. Calculate the value of $\Delta H°$ for the reaction

$$C_2H_4(g) + H_2O(l) \rightarrow C_2H_5OH(l)$$

Given the following thermochemical equations,

$$C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l);$$
$$\Delta H^\circ = -1411.1\ \text{kJ}$$
$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l);$$
$$\Delta H^\circ = -1367.1\ \text{kJ}$$

11. Calculate the maximum work that could be obtained from the combustion of 100 g of ethanol, $C_2H_5OH(l)$. How does it compare with the maximum work from the combustion of 100 g of $C_8H_{18}(l)$? Which is the better fuel?

12. The heat of vaporization of mercury is 60.7 kJ mol^{-1}. For Hg(l), $S^\circ = 76.1$ J mol^{-1} K^{-1} and for Hg(g), $S^\circ = 175$ J mol^{-1} K^{-1}. Estimate the normal boiling point of liquid mercury.

13. Suppose that you were pumping an automobile tire with a hand pump that pushed 24.0 in.^{3} of air into the tire on each stroke, and that during one such stroke the opposing pressure in the tire was 30.0 lb in.$^{-2}$ above the normal atmospheric pressure of 14.7 lb in.$^{-2}$. Calculate the number of joules of work accomplished during each stroke. (1 L atm = 101.325 J.)

14. A 10 L vessel at 20°C contains butane, $C_4H_{10}(g)$, at a pressure of 2 atm. What is the maximum amount of work that can be obtained by the combustion of this butane if the gas is first brought to a pressure of 1 atm and the temperature is brought to 25°C? Assume the products are also returned to that same temperature and pressure.

15. Calculate the entropy change when 1.8 g of water is completely converted into vapor at 100°C. The molar heat of vaporization is 40.85 kJ mol^{-1}.

16. Alcohol is oxidized to acetic acid if it is left exposed to air. The equation for the reaction is

$$C_2H_5OH(l) + O_2(g) \rightarrow HC_2H_3O_2(l) + H_2O(l)$$

Calculate ΔS° for the reaction in J K^{-1}.

17. Phosgene, $COCl_2$, reacts with the moisture in the lungs to produce HCl, which causes the lungs to fill with fluid, and CO, which asphyxiates the victim. Both lead ultimately to death. For $COCl_2(g)$, $S^\circ = 284$ J mol^{-1} K^{-1} and $\Delta H_f^\circ = -223$ kJ mol^{-1}. Use this information and the data in Table 6.3 to calculate ΔG_f° for $COCl_2(g)$ in kJ mol^{-1}.

18. Gasohol is a mixture of gasoline and ethanol (grain alcohol), C_2H_5OH. Calculate the maximum work that could be obtained at 25°C and 1 atm by burning 1 mol of C_2H_5OH.

19. For the melting of aluminum, $Al(s) \rightarrow Al(l)$, $\Delta H^\circ = 10.0$ kJ mol^{-1} and $\Delta S^\circ = 9.50$ J mol^{-1} K^{-1}. Calculate the melting point of Al. (The actual melting point is 660°C.)

20. Which of the following reactions (equations unbalanced) would be expected to be spontaneous at 25°C and 1 atm?

(a) $PbO(s) + NH_3(g) \rightarrow Pb(s) + N_2(g) + H_2O(g)$
(b) $NaOH(s) + HCl(g) \rightarrow NaCl(s) + H_2O(l)$
(c) $Al_2O_3(s) + Fe(s) \rightarrow Fe_2O_3(s) + Al(s)$
(d) $2CH_4(g) \rightarrow C_2H_6(g) + H_2(g)$

21. The reaction $CO(g) + H_2O(g) \rightleftharpoons HCHO_2(g)$ has $\Delta G^\circ_{673\,K} = +79.8$ kJ mol^{-1}. If a mixture at 400°C contains 0.04 mol CO, 0.022 mol H_2O, and 3.8×10^{-3} mol $HCHO_2$ in a 2.50 L container, is the reaction at equilibrium? If not, in which direction will the reaction proceed spontaneously?

22. The standard heat of formation of ethylene, $C_2H_4(g)$, is +52.284 kJ mol^{-1}. Calculate the C

7. Which of the following reactions represents $\Delta_{hyd}H$:

(A) $CuSO_4(s) \xrightarrow{(aq)} CuSO_4(aq); \Delta H = -x$ kJ

(B) $BaCl_2(s) + 2H_2O(l) \rightarrow BaCl_2 + 2H_2O(s); \Delta H = -y$ kJ

(C) $CuSO_4(s) + 5H_2O(l) \xrightarrow{(aq)} CuSO_4 \cdot 5H_2O(aq); \Delta H = -z$ kJ

(D) None of these

8. Which one of the following statements is false?

(A) Work is a state function.

(B) Temperature is a state function.

(C) Work appears at the boundary of the system.

(D) Change in the state is completely defined when the initial and final states are specified.

9. A gas mixture consisting of 3.67 L of ethylene and methane on complete combustion at 25°C produces 6.11 L of CO_2. Find out the amount of heat evolved on burning 1 L of the gas mixture. The heats of combustion of ethylene and methane are –1423 and –891 kJ mol^{-1}, respectively, at 25°C

(A) 30.88 kJ (B) 20.28 kJ

(C) 50.88 kJ (D) 60.18 kJ

10. If 1 kcal of heat is added to 1.2 L of oxygen in a cylinder at constant pressure of 1atm, the volume increases to 1.5 L. Hence, ΔU for this process is:

(A) 0.993 kcal (B) 1.0073 kcal

(C) 0.0993 kcal (D) 1.00073 kcal

11. For $A \rightarrow B, \Delta H = 4$ kcal mol^{-1}, $\Delta S = 10$ cal mol^{-1} K^{-1}. Reaction is spontaneous when temperature can be

(A) 400 K (B) 300 K

(C) 500 K (D) None of these.

12. If $\Delta G = \Delta H - T\Delta S$ and $\Delta G = \Delta H + T\left(\frac{d(\Delta G)}{dT}\right)_p$ then variation of EMF of a cell E, with temperature T is given by

(A) $\frac{\Delta H}{nF}$ (B) $\frac{\Delta G}{nF}$

(C) $\frac{\Delta S}{nF}$ (D) $-\frac{\Delta S}{nF}$

13. For the reaction $X_2O_4(l) \rightarrow 2XO_2(g)$, $\Delta U = 2.1$ kcal. $\Delta S = 20$ cal K^{-1} at 300 K. Then, ΔG is

(A) 2.7 kcal (B) –2.7 kcal

(C) 9.3 kcal (D) –9.3 kcal

14. From the following data of ΔH, of the following reactions,

$$C(s) + \tfrac{1}{2}O_2(g) \rightarrow CO(g); \Delta H; = -110 \text{ kJ}$$

$$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g); \Delta H -132 \text{ kJ}$$

What is the mole composition of the mixture of steam and oxygen on being passed over coke at 1273 K, keeping temperature constant.

(A) 0.5:1 (B) 0.6:1

(C) 0.8:1 (D) 1:1

15. For a reaction, A + B → AB, ΔC_p is given by the equation $40 + 5 \times 10^{-3}$ T J K^{-1} in the temperature range 300–600 K. The enthalpy of the reaction at 300 K is –25.0 kJ. Calculate the enthalpy of the reaction at 450 K. Also $S°(NO_2)$ – 57.5 cal deg^{-1}, $S°(O_2)$ – 49.0 cal deg^{-1}, $S°(NO) = 50.3$ cal deg^{-1}, $S°(O_3) = 56.8$ cal deg^{-1}.

(A) –10.12 kJ (B) –28.32 kJ

(C) –18.72 kJ (D) –8.21 kJ

16. The enthalpy of neutralization of HCl by NaOH is –55.9 kJ mol^{-1}. If the enthalpy of neutralization of HCN by NaOH is –12.1 kJ mol^{-1}, the enthalpy of dissociation of HCN is

(A) –43.8 kJ (B) 43.8 kJ

(C) 68 kJ (D) –68 kJ

17. Which of the reaction defines $\Delta H_f°$?

(A) $\tfrac{1}{2}H_2(g) + \tfrac{1}{2}F_2(g) \rightarrow HF(g)$

(B) $CO(g) + \tfrac{1}{2}O_2(g) \rightarrow CO_2(g)$

(C) $\underset{\text{Diamond}}{C} + O_2(g) \rightarrow CO_2(g)$

(D) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

18. If ΔH of a reaction is 100 kJ mol^{-1}, then the activation energy must be

(A) greater than 100 kJ mol^{-1} (B) less than 100 kJ mol^{-1}

(C) equal to 100 kJ mol^{-1} (D) none of these.

19. Heat of hydrogenation of ethene is x_1 and that of benzene is x_2. Hence resonance energy is

(A) $x_1 - x_2$ (B) $x_1 + x_2$

(C) $3x_1 - x_2$ (D) $x_1 - 3x_2$

20. Heat of neutralization of oxalic acid is –25.4 k cal mol^{-1} using strong base, NaOH. Hence, enthalpy change of the process is $H_2C_2O_4 \rightleftharpoons 2H^+ + C_2O_4^{2-}$ is

(A) 2.0 kcal (B) –11.8 kcal

(C) 1.0 kcal (D) –1.0 kcal

21. The lattice energy of NaCl is –780 kJ mol^{-1}. The enthalpies of hydration of $Na^+(g)$ and $Cl^-(g)$ ions are –406 kJ mol^{-1} and –364 kJ mol^{-1}. The enthalpy of solution of NaCl(s) is

(A) 738 kJ mol^{-1} (B) 10 kJ mol^{-1}

(C) –10 kJ mol^{-1} (D) –822 kJ mol^{-1}

22. Some of the thermodynamic parameters are state variables while some are process variables. Some groups of the parameters are given. Choose the correct one.

(A) State variables: Temperature, Number of moles
Process variables: Internal energy, work done by the gas

(B) State variables: Volume, temperature
Process variables: Internal energy, work done by the gas

(C) State variables: work done by the gas, heat rejected by the gas.
Process variables: Temperature, volume

(D) State variables: Internal energy, volume
Process variables: Work done by the gas, heat absorbed by the gas

23. Using only the following data:

$$Fe_2O_3(s) + 3CO(g) \rightleftharpoons 2Fe(s) + 3CO_2(g);$$

(I) $\Delta H° = -26.8$ kJ

$$Fe(s) + CO(g) \rightleftharpoons FeO(s) + CO(g);$$

(II) $\Delta H° = +16.5$kJ

the $\Delta H°$ value, in kilojoules, for the reaction

$Fe_2O_3(s) + CO(g) \rightarrow 2FeO(s) + CO_2(g)$ is calculated as

(A) –43.3 (B) –10.3
(C) +6.2 (D) +10.3

24. The Kirchhoff's equation gives the effect of __________ on heat of reaction.

(A) pressure (B) temperature
(C) volume (D) molecularity

25. One mole of a real gas is subjected to heating at constant volume from (p_1, V_1, T_1) state to (p_2, V_2, T_2) state. Then it is subjected to irreversible adiabatic compression against constant atmosphere till system reaches the final state (p_3, V_3, T_3). If the constant volume molar heat capacity of real gas is C_V. Find out correct expression for ΔH from state 1 to state 3.

(A) $C_V(T_3 - T_1) + (p_3V_1 - p_1V_1)$
(B) $C_V(T_2 - T_1) + (p_3V_2 - p_1V_1)$
(C) $C_V(T_2 - T_1) + (p_3V_1 - p_1V_1)$
(D) $C_p(T_2 - T_1) + (p_3V_1 - p_1V_1)$

26. In which case of mixing of a strong acid and a base, each of 1(N) concentration, temperature-increase is the highest?

(A) 20 mL acid and 30 mL alkali
(B) 10 mL acid and 40 mL alkali
(C) 25 mL acid and 25 mL alkali
(D) 35 mL acid and 15 mL alkali

27. The molar entropy of vaporization of acetic acid is 14.4 cal K^{-1} mol^{-1} at its boiling point 118°C. The latent heat of vaporization of acetic acid is

(A) 49 cal g^{-1} (B) 64cal g^{-1}
(C) 94 cal g^{-1} (D) 84 cal g^{-1}

28. The bond energies of C

(C) Work done by the gas in both the processes would be equal.

(D) Total heat given to the gas in (I) is greater than in (II).

43. $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$; ΔH_H

6. When a real gas expends adiabatically against a finite pressure,
(A) its internal energy increases.
(B) its internal energy decreases.
(C) its temperature always decreases.
(D) its entropy always remains constant.

7. Which of the following processes have positive value for ΔH?
(A) $H_2(g) \rightarrow 2H(g)$
(B) $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$
(C) $H(g) \rightarrow H^+(g) + e^-$
(D) $H_2O(l) \rightarrow H_2O(s)$

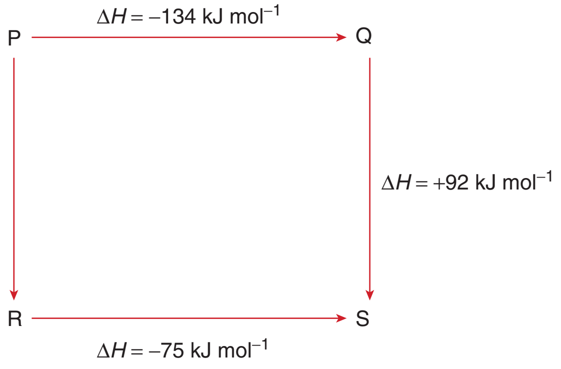
8. $C(s) + \frac{1}{2}O_2 \rightarrow CO(g)$;
$\Delta H° = -26$ kcal mol^{-1}

$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$;
$\Delta H° = -68$ kcal mol^{-1}

Which is/are correct statement(s)?
(A) heat of formation of CO_2 is –68 kcal mol^{-1}
(B) heat of combustion of C(s) is –26 kcal mol^{-1}
(C) heat of combustion of CO(g) –68 kcal mol^{-1}
(D) heat of formation of CO(g) is –26 kcal mol^{-1}

9. An adiabatic process involves
(A) no exchange of heat.
(B) exchange of heat with change in volume.
(C) work done equal to change in internal energy.
(D) increase in temperature of the system under reversible compression.

10. Figure 7.40 illustrates the energy change of a set of reactions.



$\Delta H = -134$ kJ mol^{-1}
P
Q
$\Delta H = +92$ kJ mol^{-1}
R
S
$\Delta H = -75$ kJ mol^{-1}

Figure 7.40

Which of the following statements are correct?
(A) The enthalpy change for the reaction P → R is –33 kJ mol^{-1}.
(B) The enthalpy change for the transformation R → Q will be endothermic.
(C) The enthalpy change for the transformation R → Q will be exothermic.
(D) The enthalpy change for the transformation S → P will be +42 kJ mol^{-1}.

11. Which of the following process take(s) place with decrease of entropy?
(A) $3CO_2(g) \rightarrow 2O_3(g)$
(B) Sugar + Water → Solution
(C) $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$
(D) $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$

12. Choose the incorrect combination(s).

ΔH	ΔS	Temperature (T)	Spontaneity
(a) +	–	Any T	Non-spontaneous
(b) –	–	Low T	Non-spontaneous
(c) +	+	Low T	Spontaneous
(d) –	+	Any T	Spontaneous

13. Mark out the correct one(s) about the pV plot system shown in Fig. 7.41.

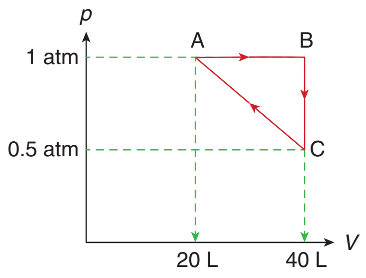


Figure 7.41

(A) The entropy change for the overall process is 0 (zero).
(B) $\Delta H > \Delta E$ for the overall process.
(C) Total work, $w = q$.
(D) Total work = –620.77 J.

14. Which of the following statements are correct?
(A) When $\Delta G = 0$, the system is at equilibrium.
(B) When $\Delta G < 0$, the process will be spontaneous.
(C) When ΔG is negative, the process is said to be exergonic.
(D) When ΔG is positive, the process is said to be endergonic.

Assertion–Reasoning Type

Choose the correct option from the following:
(A) Statement 1 is True, Statement 2 is True; Statement 2 is a correct explanation for Statement 1.
(B) Statement 1 is True, Statement 2 is True; Statement 2 is NOT a correct explanation for Statement 1.
(C) Statement 1 is True, Statement 2 is False.
(D) Statement 1 is False, Statement 2 is True.

1. Statement 1: If a system goes from state A to state B by following reversible and irreversible process respectively then change in internal energy in both the process should be same.
Statement 2: Change in internal energy is a state function.

2. **Statement 1:** As solid changes to liquid and then to vapour state, entropy increases.

   Statement 2: As going from solid to liquid and then to vapour state, disorder increases.

3. **Statement 1:** Entropy of all elements is zero at 0 K.

   Statement 2: Standard entropy of all elements is greater than zero.

4. **Statement 1:** Internal energy of a system is an extensive property.

   Statement 2: The internal energy of a system depends upon the amount and physical state of the substance

5. **Statement 1:** For an adiabatic process pV^{γ} = constant, where g is the ratio of C_p and C_V)

   Statement 2: The slope of isothermal process curve = $\gamma \times$ slope of adiabatic curve

6. **Statement 1:** The temperature of a gas does not change when it undergoes an adiabatic expansion.

   Statement 2: During an adiabatic expansion of a real gas, the internal energy of the gas remains constant.

7. **Statement 1:** If Gibbs energy change of the system is negative, the process is spontaneous even if the total Gibbs energy change of the system and the surroundings is positive.

   Statement 2: The spontaneity of a process depends only on the Gibbs energy change of the system.

8. **Statement 1:** The standard free energy of all spontaneous occurring reactions are positive because

   Statement 2: The free energies of elements standard states at 760 mm Hg and 298 K are taken as zero.

9. **Statement 1:** The enthalpy of formation of $H_2O(l)$ is greater than that of $H_2O(g)$

   Statement 2: Enthalpy change is negative for the condensation reaction : $H_2O(g) \rightarrow H_2O(l)$

10. **Statement 1:** The enthalpy of formation of gaseous oxygen molecules at 298 K and under a pressure of one atm. is zero.

    Statement 2: The entropy of formation of gaseous oxygen molecules under the same condition is zero.

11. **Statement 1:** The heat absorbed during the isothermal expansion of an ideal gas against vacuum is zero.

    Statement 2: The volume occupied by the molecules of an ideal gas is zero.

12. **Statement 1:** Heat energy is completely transformed into work during reversible isothermal expansion of an ideal gas.

    Statement 2: During a reversible isothermal process of an ideal gas, the changes in internal energy due to decrease in pressure are nullified by the changes due to increase in volume.

Comprehension Type

Read the paragraphs and answer the questions that follow.

Paragraph I

Enthalpy of neutralization is defined as the enthalpy change when 1 mol of H^+ in dilute solution combines with 1 mol of OH^- o give rise to undissociated water, that is, $H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)\ \Delta H = -57.54\ \text{kJ mol}^{-1}$ or $-13.7\ \text{kcal mol}^{-1}$. When 1 mol of strong monoprotic acid is mixed with 1 mol of strong base, the above neutralization reaction takes place.

When a weak acid/base reacts with a strong base/acid, the release of heat is less than 57.54 kJ mol^{-1}. It is because of the fact that these acids/bases are not completely ionized in the solution. Some heat is consumed in ionizing them.

1. When 1 g equiv. of NaOH reacts with 0.33 g equiv. of HCl, enthalpy change is – 4.6 cal. When 0.66 equivalent of HCl is further added, enthalpy change would be

   (A) –13.7 cal (B) –9.2 cal
   (C) 13.7cal (D) 9.2 cal

2. In the following reaction, involving neutralization of HF (a weak acid) with NaOH (a strong base).

   $$\text{HF (aq)} + \text{NaOH (aq)} \rightarrow \text{NaF(aq)} + H_2O(l);$$

   the heat of neutralization is – 68.6kJmol^{-1}
   This value is much higher than the heat of neutralization of strong acid with strong base (= –57.3 kJ mol^{-1}). This is because

   (A) in aqueous solution, HF behaves as a strong acid.
   (B) there is hydration of F^- ion in aqueous solution, and process is exothermic.
   (C) both A and B.
   (D) none of these.

3. Heat of dissociation of CH_3COOH is 0.005 kcal g^{-1}, hence enthalpy change when 1 mol of $Ca(OH)_2$ is completely neutralized by CH_3COOH is:

   (A) –27.4 kcal (B) –13.6 kcal
   (C) –26.8 kcal (D) –27.1 kcal

Paragraph II

Enthalpy of reaction is the heat change accompanying any reaction, depending upon the nature of the reaction the enthalpy of the reaction is named accordingly. For example, in the reaction

$$CH_4(g) + O_2(g) \rightarrow CO_2(g) + H_2O(l);$$
$$\Delta H = -890.4\ \text{kJ mol}^{-1}$$

This reaction shown that 890.4 kJ of heat is produced when methane is completely burnt is known as heat of combustion. For example, in the reaction

$$C(s) + O_2(g) \rightarrow CO_2(g);$$
$$\Delta H = -393.5\ \text{kJ mol}^{-1}$$

when $CO_2(g)$ is formed from its elements, that is, from C(s) and $O_2(g)$ 393.5 kJ of heat is produced and the process in heat of formation.

4. The enthalpy of formation of methane from the following data

(I) $C(s) + O_2(g) \rightarrow CO_2(g); \Delta H = -393.5\,kJ\,mol^{-1}$

(II) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l); \Delta H = -285.8\,kJ\,mol^{-1}$

(III) $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$ $\Delta H = -890.4\,kJ/mol$

(A) -74.9 kJ mol^{-1} (B) 54.6 kJ mol^{-1}
(C) 99.7 kJ mol^{-1} (D) -89.6 kJ mol^{-1}

5. Calculate the enthalpy of formation of sucrose $(C_{12}H_{22}O_{12})_n$ from the following data:

(I) $\Delta H = -5200.7$ kJ mol^{-1}
(II) $C(s) + O_2(g) \rightarrow CO_2(g); \Delta H = -393.5\,kJ\,mol^{-1}$
(III) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l);$ $\Delta H = -285.8\,kJ\,mol^{-1}$

(A) -10.3 kJ mol^{-1} (B) $+863.4$ kJ mol^{-1}
(C) -2677.1 kJ mol^{-1} (D) -4321.3 kJ mol^{-1}

6. Calculate the enthalpy of combustion of benzene from the following data:

(I) $6C(s) + 3H_2(g) \rightarrow C_6H_6(l), \Delta H = 49.0\,kJ\,mol^{-1}$
(II) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l);$ $\Delta H = -285.8\,kJ\,mol^{-1}$
(III) $C(s) + O_2(g) \rightarrow CO_2(g);$ $\Delta H = -389.3\,kJ\,mol^{-1}$

(A) $+463.6$ kJ mol^{-1} (B) $+32.4$ kJ mol^{-1}
(C) -1432.3 kJ mol^{-1} (D) -3242.2 kJ mol^{-1}

Paragraph III

Consider the following reaction $N_2O_4(g) \rightarrow 2NO_2(g)$. The Gibbs energy of the reaction occurring at 298 K and 1 atm has been plotted against the fraction of N_2O_4 dissociated as shown in Fig. 7.42.

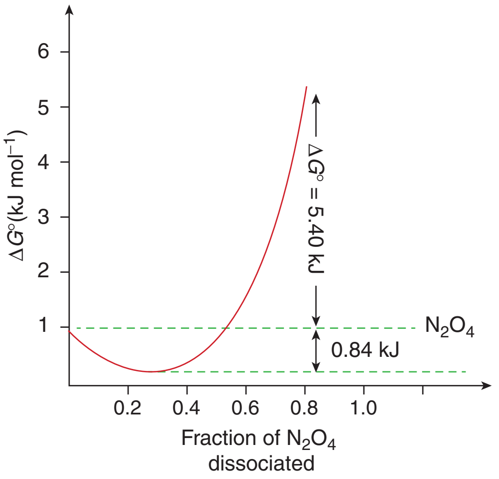


Figure 7.42

7. When two moles of NO_2 change into equilibrium mixture with N_2O_4, then ΔG^o is

(A) -5.40 kJ (B) $+5.40$ kJ
(C) -6.24 kJ (D) 6.24 kJ

8. When one mole of N_2O_4 changes into equilibrium mixture with NO_2, then ΔG^o is

(A) -5.40 kJ (B) 0.84 kJ
(C) -0.84 kJ (D) 6.24

9. Select out the correct statement.

(A) The conversion of N_2O_4 into $2NO_2$ is spontaneous.
(B) The conversion of $2NO_2$ into N_2O_4 is non-spontaneous.
(C) The attainment of equilibrium from N_2O_4 and from NO_2 are both equally spontaneous.
(D) The attainment of equilibrium from two moles of NO_2 with N_2O_4 is more spontaneous than the conversion of $2NO_2$ into N_2O_4.

Integer Answer Type

The answer is a **non-negative integer**.

1. 1 mol of monatomic perfect gas, initially at 1.0 atm pressure and at 300 K is heated reversibly to 400 K at constant volume. Calculate the change in internal energy and the work done.

2. The amount of ice (in g) that remains when 52 g of ice is added to 100 g of water at 40°C is __________.

3. Standard Gibbs energy change for a reaction is zero. The value of equilibrium constant is __________.

4. When 100 mL of each of HCl and NaOH solutions are mixed, 5.71 kJ of heat was evolved. The molarity of the solutions is __________.

5. Enthalpy of neutralization of HCl by NaOH is -57.32 kJ mol^{-1} and by NH_4OH is -51.34 kJ mol^{-1}.
Calculate the enthalpy of dissociation of NH_4OH.

6. A gas expands against a constant external pressure so that the work done is 607.8 J. The work done in liter atmosphere is __________.

7. For the equilibrium reaction, the value of Gibbs energy is __________.

Matrix Match Type

1. Match the process with the expression.

Column I	Column II
(A) For spontaneous	(p) $\sum \Delta_{\text{bond}} H(\text{reactants}) - \sum \Delta_{\text{bond}} H(\text{products})$
(B) For endothermic	(q) $\Delta_r H = \Delta_r U$
(C) For dissociation	(r) $\Delta G < 0$
(D) For solids and liquids in a thermochemical reaction (s)	$\sum H(\text{products}) > \sum H(\text{reactants})$

2. Match the gas with the ration $\gamma = C_p/C_V$.

Column I	Column II
(A) Ammonia	(p) 1.20
(B) Carbon dioxide	(q) 1.30
(C) Carbon monoxide	(r) 1.40
(D) Helium	(s) 1.66

3. Match the process with the correct expressions

Column I	Column II
(A) Isochoric process	(p) ΔS
(B) Isobaric process	(q) $\Delta q = 0$ as $\Delta E = q + w$
(C) Isothermal process	(r) $w = 0$
(D) Adiabatic process	(s) $\Delta T = 0$

4. Match the signs of ΔH and ΔS with the nature of the reaction.

Column I	Column II
(A) Negative and negative	(p) Spontaneous only at low temperature.
(B) Negative and positive	(q) Spontaneous only at high temperature.
(C) Positive and positive	(r) Spontaneous at all temperature.
(D) Positive and negative	(s) Non-spontaneous at all temperature.

5. Match the column correctly

Column I	Column II
(A) Extensive properties	(p) Density (at constant p, V and T pressure)
(B) Closed system	(q) Bursting of tyre
(C) Path function	(r) Additive in nature
(D) Adiabatic	(s) $U \neq$ constant
(E) Intensive properties	(t) Heat

ANSWERS

Review Questions

1. 25°C; 1 atm

2. A thermochemical equation contains the value for the associated ΔH.

3. If 1/2 the amount of materials reacts, 1/2 the amount of heat will be generated or required.

4. **(a)** produce one mole of a compound at 25°C and 1 atm and **(b)** the reactants must be elements in their standard states.

5. –78.61 kJ

6. Only ΔU is a state function

7. N m

8. In case **(b)**, $q < 0$ and $w < 0$ so ΔU is the most negative.

10. Spontaneous processes tend to proceed from states of low probability to states of higher probability.

13. No. Only a pure substance can have an entropy of zero, and that too only at 0 K

14. Much of the energy is lost as heat which is used to maintain our body temperature.

20. The number of moles of products versus reactants, the state of the products versus reactants and the complexity of the molecules.

21. **(a)** Positive; **(b)** negative; **(c)** negative; **(b)** negative

22. 3.91×10^3 kJ released per mole of acetone formed.

24. CF_4

26. $T\Delta S$ must be larger than the magnitude of ΔH in order to obtain a negative value for ΔG.

Numerical Problems

1. **(a)** 1.67×10^3 J; **(b)** 1.67×10^3 J; **(c)** 23.2 J°C^{-1}; **(d)** 4.64 J g^{-1}°C^{-1}

2. 1.255×10^3 J; **(b)** 1.255×10^3 J; **(c)** 34.7 g

3. 113. J mol^{-1}°C^{-1}

4. 19.24 kJ; –57.98 kJ mol^{-1}

5. **(a)** $C_7H_8(l) + 9O_2(g) \rightarrow 7CO_2(g) + 4H_2O(l)$; **(b)** 6.367×10^4 J; **(c)** 3.911×10^6 J

6. **(a)** –283 kJ; **(b)** $\frac{2}{3}NH_3(g)+\frac{7}{6}O_2(g)\rightarrow \frac{2}{3}NO_2(g)+H_2O(g); \Delta H° = -1132/6 = -189$ kJ

8. 33.8°C

9. 32°C

10. –44.0 kJ

11. The octane is a better fuel on both a per gram and per mole basis.

12. 614 K

13. 121 J

14. 16.5 kJ

15. –269.75 J K^{-1}

16. –136 J K^{-1}

17. –209 kJ mol^{-1}

18. –1299.8 kJ

19. 1.05×10^3 K

20. **(a)** and **(b)**

21. Since the value of Q is larger than the value of K_p, the system must shift to the left in order to reach equilibrium.

22. 605 kJ mol^{-1}

23. 101.325 J

24. 945.36 kJ; 498.34 kJ

Additional Objective Questions

Single Correct Choice Type

1. (A)
2. (B)
3. (D)
4. (B)
5. (A)
6. (A)
7. (C)
8. (A)
9. (C)
10. (A)
11. (C)
12. (C)
13. (B)
14. (B)
15. (C)
16. (B)
17. (A)
18. (A)
19. (C)
20. (A)
21. (B)
22. (D)
23. (C)
24. (B)
25. (C)
26. (C)
27. (C)
28. (C)
29. (A)
30. (D)
31. (D)
32. (B)
33. (B)
34. (A)
35. (B)
36. (B)
37. (B)
38. (A)
39. (B)
40. (A)
41. (C)
42. (B)
43. (C)
44. (D)
45. (B)
46. (B)
47. (C)
48. (C)
49. (A)
50. (B)

Multiple Correct Choice Type

1. (A), (B), (D)
2. (A), (B)
3. (C), (D)
4. (A), (B)
5. (A), (B), (C)
6. (B), (C), (D)
7. (A), (C)
8. (C), (D)
9. (A), (B), (C)
10. (C), (D)
11. (A, C)
12. (B, C)
13. (A, D)
14. (A, B, C, D)

Assertion – Reasoning Type

1. (A)
2. (A)
3. (A)
4. (A)
5. (C)
6. (D)
7. (A)
8. (D)
9. (A)
10. (C)
11. (D)
12. (C)

Comprehension Type

1. (B)
2. (B)
3. (D)
4. (A)
5. (C)
6. (D)
7. (C)
8. (C)
9. (D)

Integer Answer Type

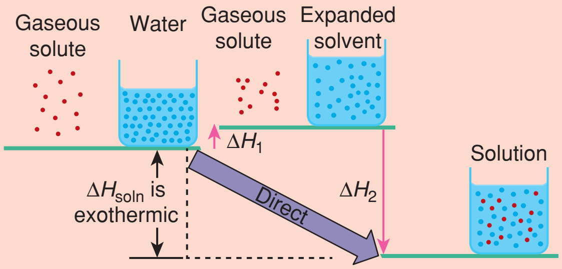
1. (0)
2. (2)
3. (1)
4. (1)
5. (6)
6. (6)
7. (0)

Matrix–Match Type

1. A $\rightarrow$(r); B $\rightarrow$ (s); C $\rightarrow$ (p); D $\rightarrow$ (q)
2. A $\rightarrow$ (s); B $\rightarrow$ (r); C $\rightarrow$ (q); D $\rightarrow$ (p)
3. A $\rightarrow$ (r); B $\rightarrow$ (s); C $\rightarrow$ (p, s); D $\rightarrow$ (q, s)
4. A $\rightarrow$ (p); B $\rightarrow$ (r); C $\rightarrow$ (q); D $\rightarrow$ (s)
5. A $\rightarrow$(r); B $\rightarrow$ (t); C $\rightarrow$ (s); D $\rightarrow$ (q); E $\rightarrow$ (p)

8

Solutions



A molecular model of gas solubility

Contents

8.1 Type of Solutions
8.2 Solubility
8.3 Effect of Nature of Solute and Solvent
8.4 Effect of Temperature on Solubility
8.5 Effect of Pressure on Solubility of Gases
8.6 Different Methods for Expressing Concentration of Solution
8.7 Vapor Pressure of Solutions
8.8 Enthalpy of Solution
8.9 Ideal Solutions
8.10 Non-Ideal Solutions
8.11 Colligative Properties and Determination of Molar Mass
8.12 Abnormal Molar Masses and van't Hoff Factor

The term **solution** is used in chemistry to describe a system in which one or more substances are **homogeneously** mixed or dissolved in another substance. A simple solution has two components: a solute and a solvent. The **solute** is the component that is dissolved or is the least abundant component in the solution. Solutes can be solids, like sugar dissolved in lemonade or the salts dissolved in sea water. Some solutes are liquid, like ethylene glycol dissolved in water to protect a vehicle's radiator against freezing. Solutes, of course, can be gases, like carbon dioxide dissolved in carbonated beverages. The **solvent** is the dissolving agent or the most abundant component in the solution. When water is a component of a solution, it is usually considered to be the solvent even when it is present in small amounts and the solution is known as aqueous solution.

In this chapter, we will study not only aqueous solutions, but also solutions involving other solvents. We will concentrate on liquid solutions, although solutions can also be gaseous or solid. In fact, all gases mix completely at the molecular level. Solid solutions of metals are called alloys, for example, brass, bronze, etc.

8.1 | TYPE OF SOLUTIONS

There is a wide variation in the ability of liquids to dissolve different solutes. For example, when salt is dissolved in water to form a solution, it is the solute and water is the solvent; and the mixture is called a **binary solution** (because there are two constituents). Complex solutions containing more than one solute and/or more than one solvent are also common. The three states of matter—solid, liquid and gas—give us nine different types of solutions: solid dissolved in solid, solid dissolved in liquid, solid dissolved in gas, liquid dissolved in liquid and so on. Of these, the most common solutions are solid dissolved in liquid, liquid dissolved in liquid, gas dissolved in liquid, and gas dissolved in gas. Some common types of solutions are listed in Table 8.1.

Table 8.1 Common types of solutions

Solute + solvent	Solution	Example
Solid in solid	Solid	Alloys, gemstones etc.
Solid in liquid	Liquid	Sugar in water
Solid in gas	Gaseous	Camphor in nitrogen gas
Liquid in solid	Solid	Mercury with sodium/silver
Liquid in liquid	Liquid	Ethanol in water
Liquid in gas	Gaseous	Water in air
Gas in solid	Solid	Solution of hydrogen in palladium
Gas in liquid	Liquid	O_2 dissolved in water
Gas in gas	Gaseous	Air

A **true solution** is one in which the particles of dissolved solute are molecular or ionic in size, generally in the range of 0.1 nm to 1 nm (10^{-8} cm to 10^{-7} cm). The properties of a true solution are as follows:

1. A homogeneous mixture of two or more components (solute and solvent) and has a variable composition; that is, the ratio of solute to solvent can be varied.
2. The dissolved solute is molecular or ionic in size.
3. It is either colored or colorless and is usually transparent.
4. The solute remains uniformly distributed throughout the solution and does not settle down with time.
5. The solute can generally be separated from the solvent by purely physical means (e.g., by evaporation).

Solved Example 8-1

Which of the following not a true homogeneous solution: H_2 in Pt, Smoke, Air and Salt in water?

Solution

Smoke contains solid particles in gaseous solvent, and thus is not a true homogeneous solutions as the composition is not uniform throughout.

Solved Example 8-2

Give an example of a solution in which

(a) the solute is a solid and the solvent is a liquid.

(b) the solute is a gas and the solvent is a gas.

Solution

(a) Salt in water

(b) O_2 in the air

Solved Example 8-3

Match the columns and select the correct order?

(A) Solid in gas	(p) Hg in Na
(B) Liquid in solid	(q) Foam rubber
(C) Solid in solid	(r) Camphor in N_2 gas
(D) Gas in solid	(s) bronze

Solution

A → (q); B → (p); C → (s); D → (r)

Hg is the liquid solute in solid solvent Na.

Foam is the gas solute in solid solvent rubber.

Camphor is the solid solute in gaseous solvent N_2.

Bronze is an alloy of copper and tin and hence a solid in solid solution.

Solved Example 8-4

Saliva has some characteristics of a solution. Explain.

Solution

Saliva is a homogenous mixture of ionic compounds, proteins, and nucleic acids.

8.2 | SOLUBILITY

Usually, there is a limit to the amount of a solute that can dissolve in a given amount of solvent at a given temperature. When this limit is reached, we have a **saturated solution** and any excess solute that's added simply sits at the bottom of the solution. The **solubility** of a solute is the amount required to give a saturated solution, usually expressed as grams dissolved in 100 g of *solvent* at a given temperature. The temperature must be specified because solubilities vary with temperature.

The term solubility thus describes the amount of one substance (solute) that will dissolve in a specified amount of another substance (solvent) under stated conditions. For example, 36.0 g of sodium chloride will dissolve in 100 g of water at 20°C. We say then that the solubility of NaCl in water is 36.0 g/100 g H_2O at 20°C. The solubility is generally expressed in terms of mass of solute dissolved in 100 mass units of the solvent. Solubility is often used in a relative way. For instance, we say that a substance is very soluble, moderately soluble, slightly soluble or insoluble. Although these terms do not accurately indicate how much solute will dissolve, they are frequently used to describe the solubility of a substance qualitatively.

Two other terms often used to describe solubility are *miscible* and *immiscible.* Liquids that are capable of mixing and forming a homogeneous solution are **miscible**; those that do not form solutions or are generally insoluble in each other are **immiscible**. Methyl alcohol and water are miscible in each other in all proportions. Oil and water are immiscible, forming two separate layers when they are mixed.

The term *solubility* also means that the mass of solute forms a **saturated** solution with a given mass of solvent at a specified temperature. The units often are grams of solute per 100 g of solvent. It is mathematically expressed as

$$\text{Solubility} = \frac{\text{Mass of solute}}{\text{Mass of solvent}} \times 100 \tag{8.1}$$

In a saturated solution, there is an equilibrium between the undissolved solute and the solute dissolved in the solution.

$$\text{Solute (undissolved)} \rightleftharpoons \text{Solute (dissolved)}$$

When these two opposing processes are occurring at the same rate, the amount of solute in solution is constant, and a condition of equilibrium is established between dissolved and undissolved solutes. Therefore, a **saturated solution** contains dissolved solute in equilibrium with undissolved solute. It is important to state the temperature of a saturated solution, because a solution that is saturated at one temperature may not be saturated at another.

If the temperature of a saturated solution is changed, the equilibrium is disturbed, and the amount of dissolved solute will change to re-establish equilibrium. At any given temperature, a saturated solution contains the maximum amount of solute dissolved in a given amount of a solvent. A saturated solution can be conveniently prepared by dissolving a little more than the saturated amount of solute at a temperature somewhat higher than room temperature. Then the amount of solute in solution will be in excess of its solubility at room temperature, and, when the solution cools, the excess solute will crystallize, leaving the solution saturated.

An **unsaturated solution** contains less solute per unit of volume than does its corresponding saturated solution. In other words, additional solute can be dissolved in an unsaturated solution without altering any other conditions. In an unsaturated solution, more amount of solute needs to be added to make it saturated. If an unsaturated solution is cooled, some amount of solute separates from the solution, thereby making the solution saturated. Conversely, on heating a saturated solution, the equilibrium gets disturbed, and the undissolved solute gets dissolved, thereby making the solution unsaturated.

In some circumstances, solutions can be prepared that contain more solute than needed for a saturated solution at a particular temperature. These solutions are said to be **supersaturated**. However, we must qualify this definition by noting that a supersaturated solution is unstable. Disturbances, such as jarring, stirring, scratching the walls of the container, or dropping in a "seed" crystal, cause the supersaturation to return to saturation, releasing heat. When a supersaturated solution is disturbed, the excess solute crystallizes out rapidly, returning the solution to a saturated state. Supersaturated solutions are not easy to prepare but may be made from certain substances by dissolving, in warm solvent, an amount of solute greater than that needed for a saturated solution at room temperature. The warm solution is then allowed to cool very slowly.

Factors Affecting Solubility

The various factors affecting solubility are as follows:

1. **Particle size:** A solid can dissolve only at the surface that is in contact with the solvent. Since surface-to-volume ratio increases as size decreases, smaller crystals dissolve faster than the larger ones.
2. **Nature of solute and solvent:** This is governed by the rule "like dissolves like" in molecular and ionic solutions. For gases, the solubility depends upon the critical temperature specific to a gas. Higher the critical temperature more will be the solubility.
3. **Concentration of the solution:** When the solute and solvent are first mixed, the rate of dissolving is at its maximum. As the concentration of the solution increases and the solution becomes more nearly saturated with the solute, the rate of dissolving decreases greatly. This rate is plotted in Fig. 8.1.
4. **Agitation or stirring:** The effect of agitation or stirring is kinetic. When a solid is first put into water, it comes in contact only with solvent in its immediate vicinity. As the solid dissolves, the amount of dissolved solute around the solid becomes more and more concentrated, and the rate of dissolving slows down. If the mixture is not stirred, the dissolved solute diffuses very slowly through the solution. Stirring distributes the dissolved solute rapidly through the solution, and more solvent is brought into contact with the solid, causing it to dissolve more rapidly.

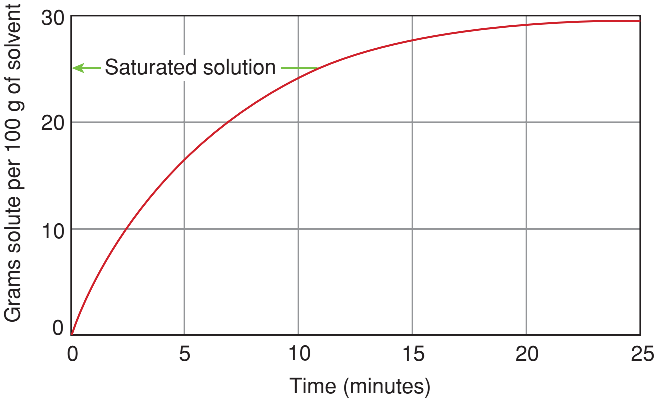


Figure 8.1 Rate of dissolution of a solid solute in a solvent.

5. **Temperature:** In most cases, the rate of dissolving of a solid increases with temperature. This increase is due to kinetic effects. The solvent molecules move more rapidly at higher temperatures and strike the solid surfaces more often, causing the rate of dissolution to increase. For gases, however, the solubility decreases with increase in temperature.
6. **Pressure:** This is generally applicable to solubility of gases and is governed by Henry's law.

8.3 | EFFECT OF NATURE OF SOLUTE AND SOLVENT

The drive to attain the most probable state favors the formation of any solution. What limits the ability of most substances to mix completely, however, are intermolecular forces of attraction. Such attractions are negligible in gases, so regardless of the chemical makeup of the molecules, the forces are unable to prevent them from mixing. That is why all gases spontaneously form solutions with each other. In liquids and solids, however, the situation is much different because intermolecular attractions are so much stronger.

For a liquid solution to form, there must be a balance among the attractive forces so the natural tendency of particles to intermingle can proceed. In other words, the attractive forces between molecules within the solvent and between molecules within the solute must be about as strong as attractions between solute and solvent molecules.

A general rule termed as “Like dissolves like” was formulated, by which solubility of the two types of solutions were studied. The rule has long enabled chemists to use chemical composition and molecular structure to predict the likelihood of two substances dissolving in each other.

1. **Molecular solutions:** When solute and solvent have molecules “like” each other in polarity, they tend to form a solution. When solute and solvent molecules are quite different in polarity, solutions of any appreciable concentration do not form. For example, water and benzene (C_6H_6) are insoluble in each other. In water, there are strong hydrogen bonds between the molecules; in benzene the molecules attract each other by relatively weak London forces and are not able to form hydrogen bonds. On the other hand, water and ethanol (C_2H_5OH) are miscible; they are soluble in all proportions. This is because water and ethanol molecules can form hydrogen bonds with each other that are nearly equivalent to those in the separate pure liquids (Fig. 8.2).

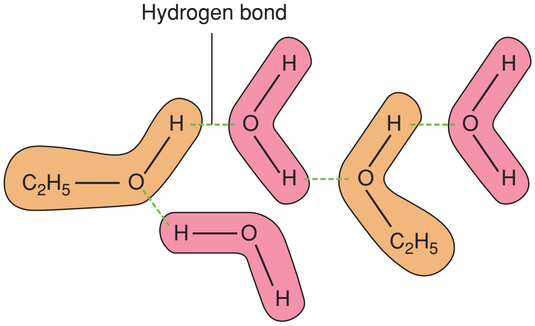
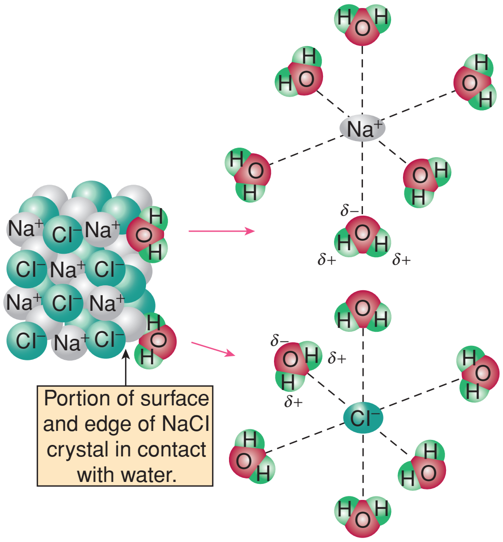


Figure 8.2 Hydrogen bonds in aqueous ethanol.

2. **Ionic solutions:** The “like dissolves like” principle also applies to the solubility of solids in liquid solvents. Polar solvents tend to dissolve polar and ionic compounds, whereas non-polar solvents tend to dissolve non-polar compounds. The solubility in case of ionic compound is explained in terms of dielectric constant of the solvent, hydration and lattice enthalpies.

   Figure 8.3 depicts a section of a crystal of NaCl in contact with water. The dipoles of water molecules orient themselves so that the negative ends of some point toward Na^+ ions and the positive ends of others point at Cl^- ions. In other words, *ion–dipole* attractions occur that tend to tug and pull ions from the crystal. At the corners and edges of the crystal, ions are held by fewer neighbors within the solid and so are more readily dislodged than those elsewhere on the crystal’s surface. As water molecules dislodge these ions, new corners and edges are exposed, and the crystal continues to dissolve.

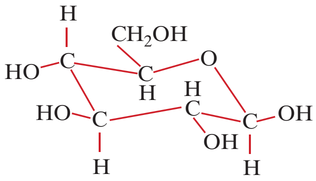


Portion of surface and edge of NaCl crystal in contact with water.

Figure 8.3 Hydration of ions.

As they become free, the ions become completely surrounded by water molecules (also shown in Fig. 8.3). The phenomenon is called the hydration of ions. The *general* term for the surrounding of a solute particle by solvent molecules is solvation, so hydration is just a special case of solvation. Ionic compounds are able to dissolve in water when the attractions between water dipoles and ions overcome the attractions of the ions for each other within the crystal.

Similar events explain why solids composed of polar molecules, like those of sugar, dissolve in water. Attractions between the solvent and solute dipoles help to dislodge molecules from the crystal and bring them into solution. Again we see that “like dissolves like”; a polar solute dissolves in a polar solvent. Sugar molecules such as the one right have polar OH groups that interact with water by hydrogen bonding.



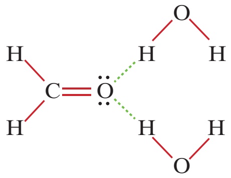
The same reasoning explains why non-polar solids like wax are soluble in non-polar solvents such as benzene. Wax is a solid mixture of long chain hydrocarbons, held together by London forces. The attractions between benzene molecules are also London forces, of comparable strength, so molecules of the wax can easily be dispersed among those of the solvent.

Note: The solubility of gases in liquids depends upon the critical temperature specific to a particular gas. For example, carbon dioxide and ammonia have higher critical temperatures than hydrogen or helium, and hence are more soluble in water, that is, they are more liquefiable.

Solved Example 8-5

Formaldehyde (H_2CO) dissolves in water without formation of ions. Write the Lewis structure of formaldehyde and show what types of interactions between solute and solvent are involved.

Solution



There is hydrogen bonding between solute and solvent.

Solved Example 8-6

Explain how ion–dipole forces help to bring potassium chloride into solution in water.

Solution

The dipole moments of water molecules can be oriented so as to stabilize both the dissolved cation and the dissolved anion.

Solved Example 8-7

Explain why potassium chloride will not dissolve in carbon tetrachloride, CCl_4.

Solution

There is no solvating force provided by carbon tetrachloride that can overcome and offset the very strong ion–ion forces of the solid KCl sample.

8.4 | EFFECT OF TEMPERATURE ON SOLUBILITY

On changing the temperature of the mixture, the equilibrium gets disturbed and either more solute will dissolve or some will precipitate out. To analyze how temperature affects solubility we can use **Le Chatelier's principle**. According to this principle, *if a system at equilibrium is disturbed, the system will change in a direction that counteracts the disturbance and causes the system to return to equilibrium*.

1. **Solubility of solid in liquid:** To increase the temperature of a solution, heat (energy) is added. When solute dissolves in a solvent, heat is absorbed or evolved. Let us consider a common situation where energy is absorbed when additional solute is dissolved in an already saturated solution.

$$\text{Solute}_{\text{undissolved}} + \text{energy} \rightleftharpoons \text{Solute}_{\text{dissolved}}$$

Now, according to Le Chatelier's principle, when we add heat energy to raise the temperature, the system responds by consuming some of the energy added. This causes the equilibrium to shift to the right. In other words, more solute dissolves and when equilibrium is re-established, there is more solute dissolved in the solution. Thus, *when dissolving more solute in a saturated solution is endothermic, raising the temperature increases the solubility of the solute*. This is a common situation for solids dissolving in liquid solvents. Figure 8.4 shows how much the solubility is affected by temperature varies for various substances.

Note: Some solutes, such as lithium sulphate, Li_2SO_4, become *less* soluble with increasing temperature (Fig. 8.4). Energy must be *released* from a saturated solution of Li_2SO_4 to make more solute dissolve. For its equilibrium equation, we must show "energy" on the right side because heat is released when more of the solute dissolves into a saturated solution.

$$\text{Solute}_{\text{undissolved}} \rightleftharpoons \text{Solute}_{\text{dissolved}} + \text{energy}$$

2. **Solubility of gas in liquid:** The solubility of a gas in water usually decreases with increasing temperature. The tiny bubbles that form when water is heated are due to the decreased solubility of air at higher temperatures. The decreased solubility of gases at higher temperatures is explained by assuming that, in order to dissolve, the gas molecules must form bonds of some sort with the molecules of the liquid. An increase in temperature decreases the solubility of the gas because it increases the kinetic energy (speed) of the gas molecules, and thereby decreases their ability to bond with the liquid molecules. (The "bond" between gaseous molecules and water/solvent molecules is very weak/poor. In fact, it is of the type of dispersion forces in most cases.) The decreased solubility at increased temperatures can also be explained on the basis of Le Chatelier's principle. Since dissolution is an **exothermic process**, increase in temperature leads to lowering of dissolution.

Table 8.2 gives data for the solubilities of several common gases in water at different temperatures, but all at one atmospheric pressure. In water, gases are usually more soluble at colder temperatures. But the solubility of gases, like other solubilities, can increase or decrease with temperature, depending on the nature of a gas and the nature of a solvent. For example, the solubilities of H_2, N_2, CO, He and Ne actually rise with rising temperature in common organic solvents like carbon tetrachloride, toluene and acetone.

Table 8.2 Solubilities of common gases in water[a]

	Temperature			
Gas	0°C	20°C	50°C	100°C
Nitrogen, N_2	0.0029	0.0019	0.0012	0
Oxygen, O_2	0.0069	0.0043	0.0027	0
Carbon dioxide, CO_2	0.335	0.169	0.076	0
Sulphur dioxide, SO_2	22.8	10.6	4.3	1.8[b]
Ammonia, NH_3	89.9	51.8	28.4	7.4[c]

[a] Solubilities are *n* grams of solute per 100 g of water when the gaseous space over the liquid is saturated with the gas and the total pressure is 1 atm.
[b] Solubility at 90°C.
[c] Solubility at 96°C.

The gases sulphur dioxide, ammonia, and, to a lesser extent, carbon dioxide are far more soluble in water than are oxygen or nitrogen (see Table 8.2). This is partly because SO_2, NH_3 and CO_2 molecules have polar bonds and sites of partial charge that attract water molecules, forming hydrogen bonds to help hold the gases in solution. Ammonia molecules, in addition, not only can accept hydrogen bonds from water (O—H---N) but also can donate them through their N—H bonds (N—H---O).

The more soluble gases also react with water to some extent as the following chemical equilibria show.

$$CO_2(aq) + H_2O \rightleftharpoons H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$
$$SO_2(aq) + H_2O \rightleftharpoons H^+(aq) + HSO_3^-(aq)$$
$$NH_3(aq) + H_2O \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

The forward reactions contribute to the higher concentrations of the gases in solution, as compared to gases such as O_2 and N_2 that do not react with water at all. Gaseous sulphur trioxide is very soluble in water because it reacts *quantitatively* (i.e., completely) with water to form sulphuric acid.

$$SO_3(g) + H_2O \rightleftharpoons H_2SO_4(aq)$$

Solved Example 8-8

Referring to Fig. 8.4, determine whether each of the following solutions is saturated, unsaturated, or supersaturated. (All are in 100 g of H_2O.)

(a) 40 g of KNO_3 at 40°C **(b)** 40 g of KNO_3 at 20°C

(c) 75 g of NH_4Cl at 80°C **(d)** 20 g of NaCl at 40°C

Solution

(a) Unsaturated **(b)** Supersaturated

(c) Saturated **(d)** Unsaturated

Solved Example 8-9

A 500 mL portion of water is saturated with Li_2SO_4 at 0°C. What happens if the solution is heated to 100°C? (Refer to Fig. 8.4)

Solution

A specific amount of Li_2SO_4 will precipitate unless the solution becomes supersaturated.

$$500\text{ g H}_2\text{O}\times\frac{35\text{ g}}{100\text{ g H}_2\text{O}}-\left(500\text{ g H}_2\text{O}\times\frac{28\text{ g}}{100\text{ g H}_2\text{O}}\right)=$$

$$175-140=35\text{ g LiSO}_4\text{ (precipitate)}$$

Solved Example 8-10

A mixture is composed of 10 g of KNO_3 and 50 g of KCl. What is the approximate amount of KCl that can be separated using the difference in solubility shown in Fig. 8.4.

Solution

Dissolve the mixture in 100 g of H_2O and heat to over 45°C. Cool to 0°C where the solution is saturated with about 10 g of KNO_3 and about 25 g of KCl. 50 – 25 = 25 g of KCl precipitates.

8.5 | EFFECT OF PRESSURE ON SOLUBILITY OF GASES

Small changes in pressure have a marked effect on the solubility of gases in liquids. The solubility of a gas in a liquid is directly proportional to the pressure of that gas above the solution. Thus, the amount of a gas dissolved in solution will double if the pressure of that gas over the solution is doubled. For example, carbonated beverages contain dissolved carbon dioxide under pressures greater than atmospheric pressure. When a can of carbonated soda is opened, the pressure is immediately reduced to the atmospheric pressure, and the excess dissolved carbon dioxide bubbles out of the solution. To understand the increase in solubility of gas with increase in pressure at the molecular level, imagine the following equilibrium established in a closed container fitted with a movable piston [Fig. 8.5(a)].

$$\text{Gas} + \text{Solvent} \rightleftharpoons \text{Solution}$$

If the piston is pushed down [Fig. 8.5(b)], the gas is compressed and its pressure increases. This causes the concentration of the gas molecules over the solution to increase, so the rate at which the gas dissolves is now greater than the rate at which it leaves the solution. Eventually, equilibrium is re-established when the concentration of the gas in the solution has increased enough to make the rate of escape equal to the rate at which the gas dissolves [Fig. 8.5(c)]. At this point, the concentration of gas in the solution is larger than before. More gas has dissolved and equilibrium is restored.

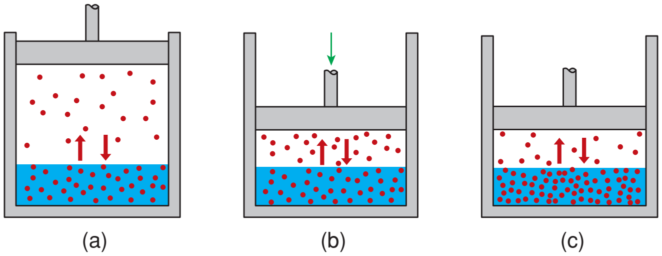


Figure 8.5 How pressure increases the solubility of a gas in a liquid with increase in pressure.

The effect of pressure on the solubility of a gas can also be explained by Le Chatelier's principle. In this case, the disturbance is an increase in the pressure of the gas above the solution. How could the system counteract the pressure increase? The answer is, by having more gas dissolved in the solution. In this way, the pressure of the gas is reduced and the concentration of the gas in the solution is increased. In other words, increasing the pressure of the gas will cause the gas to become more soluble.

Henry's Law Relates Gas Solubility to Pressure

Figure 8.6 shows how the solubility of oxygen and nitrogen in water vary with pressure. The straight lines on the graph indicate that the concentration of the gas is directly proportional to its pressure above the solution. This is expressed quantitatively by **Henry's law** (also called the **Pressure–Solubility law**) which states that *the concentration of a gas dissolved in a given volume in a liquid at any given temperature is directly proportional to the partial pressure of the gas over the solution.*

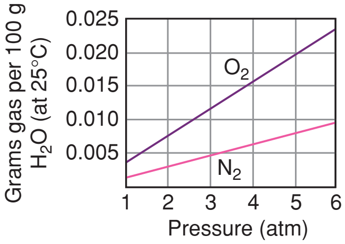


Figure 8.6 Solubility in water vs. pressure for two gases.

Mathematical Derivation of Henry's Law

According to Henry's law the mass of gas (W_{gas}) dissolved in a solvent of mass (W_{solvent}) at equilibrium pressure of gas = p, is given by

$$W_{\text{gas}} = Kp$$

Dividing both sides by W_{solvent}, we get

$$\frac{W_{\text{gas}}}{W_{\text{solvent}}} = \frac{Kp}{W_{\text{solvent}}}$$

Let

$$\frac{K}{W_{\text{solvent}}} = K_1 = \text{constant}$$

Then

$$\frac{W_{\text{gas}}/M_{\text{gas}}}{W_{\text{solvent}}/M_{\text{solvent}}} = \left(K_1 \frac{M_{\text{solvent}}}{M_{\text{gas}}}\right) p = K_2 p$$

where $K_2 = K_1 \dfrac{M_{\text{solvent}}}{M_{\text{gas}}} = \text{constant}$, M_{gas} = molecular weight of gas and M_{solvent} = molecular weight of the solvent.

Therefore,

$$\frac{n_{\text{gas}}}{n_{\text{solvent}}} = K_2 p \qquad (8.2)$$

Now

$$x_{\text{gas}} = \frac{n_{\text{gas}}}{n_{\text{gas}} + n_{\text{solvent}}}$$

where x_{gas} is the mole fraction of the gas.
Now if the solution is very dilute, then $n_{\text{gas}} \ll n_{\text{solvent}}$. Therefore

$$x_{\text{gas}} = \frac{n_{\text{gas}}}{n_{\text{solvent}}} \qquad (8.3)$$

Substituting Eq. (8.3) in Eq.(8.2), we get

$$x_{\text{gas}} = K_2 p$$

$$p = \left(\frac{1}{K_2}\right) x_{\text{gas}} = K_{\text{H}} x_{\text{gas}}$$

where K_{H} is Henry's law constant.

Around the time Henry stated this law, Dalton, in an independent study, found that solubility of a gas in a solution is directly proportional to the partial pressure of the gas. If mole fraction is used as a measure of the amount of gas dissolved in the solution (solubility), then Dalton's observations can be stated as mole fraction of a gas in the solution is proportional to the partial pressure of the gas over the solution. Henry's law can also be expressed in terms of mole fraction as "the partial pressure of the gas in vapor phase is proportional to the mole fraction of the gas in the solution". Mathematically, it can be expressed as

$$p = K_H x \tag{8.4}$$

where p is the partial pressure, x is the mole fraction and K_H is the Henry's law constant. The units of K_H depend on the units used for concentration and pressure. A plot of partial pressure vs. the mole fraction of any component B in a solution A is a straight line and the slope is equal to K_H (Fig. 8.7).

Henry's law constant K_H is different for every gas, temperature and solvent (Table 8.3). For a given gas, it is different at different temperatures; and at a given temperature, it is different for different gases. At a given pressure, higher the value of K_H for the gas, lower will be its solubility in the solution. The value of K_H generally increases with increase in temperature and hence the solubility of gas decreases with increase in temperature.

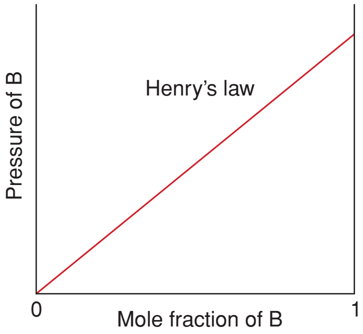


Figure 8.7 Plot of partial pressure of any component B in a solution A vs. its mole fraction.

Table 8.3 K_H values for various substances

Substance	K_H(mol L^{-1} atm^{-1})	Substance	K_H(mol L^{-1} atm^{-1})
Oxygen O_2	1.3×10^{-3}	Helium	3.7×10^{-4}
Hydrogen H_2	7.8×10^{-4}	Neon	4.5×10^{-4}
Ammonia NH_3	5.9×10^{1}	Argon	1.4×10^{-3}
Nitrogen N_2	6.5×10^{-4}	Carbon dioxide	3.4×10^{-2}
Hydrogen chloride HCl	1.9×10^{1}	Methane	9.2×10^{-3}
Molecular Cl_2	9.1×10^{-2}	Formaldehyde HCHO	6.0×10^{3}
Molecular bromine Br_2	7.9×10^{-1}	Vinyl chloride CH_2CHCl	1.8×10^{-2}

Applications of Henry's Law

Henry's law can explain many biological phenomena and finds many applications in industry. Some of these are discussed as follows:

1. The aquatic life survives better in cold water rather than in warm water. This is because the solubility of dissolved oxygen in water bodies is more at lower temperatures, which supports aquatic life better.
2. Oxygen cylinders are an essential part of mountaineers' kit and equipment. This is because at high altitudes the partial pressure of oxygen in air is less than at the ground level. This causes oxygen levels to drop in blood and tissues. The climbers feel weak and sometimes disoriented (a condition known as anoxia). To prevent this, mountaineers supplement the oxygen supply from the oxygen cylinder.
3. The air tanks also form an essential part of scuba divers' equipment. However, these tanks are filled with air diluted with helium, that is, helium (11.7%), nitrogen (56.2%) and oxygen (32.1%). This is so because, as they dive deeper into water, the level of dissolved gases is high due to high pressure. At higher pressure, the diver's body will absorb more gases. At great depths, the amount of nitrogen (and other gases) absorbed into the blood and tissue is greater than the amount absorbed at shallow depths. Oxygen is used up by cellular processes, but nitrogen is inert and just collects in the tissues. When the diver begins to ascend and the pressure under his body reduces, this makes the nitrogen less soluble in the tissues. If the diver comes up too fast (releases the pressure too fast), nitrogen comes out in the form of bubbles. This condition is known as decompression sickness, also called the

"bends". So, to avoid decompression sickness and toxic effects of high concentration of nitrogen in blood, a diver must use air tank filled with diluted air.

4. Carbonated drink bottles and cans are sealed under high pressure to increase the solubility of carbon dioxide. Before the bottle is opened, the gas above the drink is almost pure carbon dioxide at a pressure slightly higher than atmospheric pressure. When the bottle is opened, the pressure is lowered and solubility of gas in solution is also lowered; as a result some of this gas escapes with a hiss and some of the dissolved carbon dioxide also comes out of solution as bubbles. If the drink is left in the open, the concentration of carbon dioxide in solution slowly decreases till it is in equilibrium with the carbon dioxide in air and the drink becomes flat.

Solved Example 8-11

At 20°C the solubility of N_2 in water is 0.0150 g L^{-1} when the partial pressure of nitrogen is 580 torr. What will be the solubility of N_2 in water at 20°C when its partial pressure is 800 torr? Calculate your answer to three significant figures.

Solution

This problem deals with the effect of gas pressure on gas solubility, so Henry's law applies. We use this law in its form given by Equation $C_1/p_1 = C_2/p_2$ because it lets us avoid having to know or calculate the Henry's law constant. Let us gather the data first. $C_1 = 0.0150\text{ g L}^{-1}$, $C_2 = ?$, $p_1 = 580$ mm Hg, $p_2 = 800$ mm Hg. Using Equation $C_1/p_1 = C_2/p_2$, we have

$$\frac{0.0150\text{ g L}^{-1}}{580\text{ mm Hg}} = \frac{C_2}{800\text{ mm Hg}}$$

Solving for C_2, we get

$$C_2 = 0.0207\text{ g L}^{-1}$$

The solubility under the higher pressure is 0.0207 g L^{-1}.

Solved Example 8-12

Henry's law constant for the molality of methane in benzene at 298 K is 4.27×10^5 mm Hg. Determine the solubility of methane in benzene at 298 K under 760 mm Hg.

Solution

Given that $K_H = 4.27 \times 10^5$ mm Hg. Now from Henry's law, we have $p = K_H \times x$ where x is the mole fraction. Hence.

$$x = \frac{p}{K_H} = \frac{760}{4.27 \times 10^{-5}} = 1.78 \times 10^{-3}$$

Solved Example 8-13

Two unopened bottles of carbonated water are at the same temperature. If one is opened at the top of a mountain and the other at sea level, which will produce more bubbles? Explain.

Solution

The bottle opened at the top of the mountain will produce more bubbles. The solubility of a gas in a liquid decreases and, because the atmospheric pressure is lower at the top of the mountain, more gas will bubble out of solution.

8.6 | DIFFERENT METHODS FOR EXPRESSING CONCENTRATION OF SOLUTION

The concentration of a solution expresses the amount of solute dissolved in a given quantity of a solvent. Since reactions are often conducted in solution, it is important to understand the methods of expressing concentration and to know how to prepare solutions of particular concentrations. The concentration of a solution may be expressed qualitatively or quantitatively.

Qualitatively, concentration can be expressed as **dilute** or **concentrated**. When we say that a solution is *dilute* or *concentrated,* we are expressing, in a relative way, the amount of solute present. The term **dilute solution**, then, describes a solution that contains a relatively small amount of dissolved solute. Conversely, a **concentrated solution** contains a relatively large amount of dissolved solute.

Quantitatively, concentration may be expressed in any of the following ways:

1. **Mass percentage (*w*/*w*):** This method expresses the concentration of the solution as the percent of solute in a given mass of solution. It says that for a given mass of solution, a certain percent of that mass is solute. Suppose we take a bottle from the reagent shelf that reads "10% sodium hydroxide, NaOH". This statement means that for every 100 g of this solution, 10 g will be NaOH and 90 g will be water. (Note that this mass of the solution is 100 g, not 100 mL.) We could also make the same concentration of solution by dissolving 2.0 g of NaOH in 18 g of water. Mass percent concentrations are most generally used for solids dissolved in liquids:

$$\text{Mass percent} = \frac{\text{g solute}}{\text{g solute} + \text{g solvent}} \times 100 = \frac{\text{g solute}}{\text{g solution}} \times 100 \qquad (8.5)$$

Note: Note that mass percent is independent of the formula for the solute.

2. **Volume percentage (*V*/*V*):** Solutions that are formulated from two liquids are often expressed as *volume percent* with respect to the solute. The volume percent is the volume of a liquid in 100 mL of solution. The label on a bottle of ordinary rubbing alcohol reads "isopropyl alcohol, 70% by volume". Such a solution could be made by mixing 70 mL of alcohol with water to make a total volume of 100 mL, but we cannot use 30 mL of water, because the two volumes are not necessarily additive:

$$\text{Volume percent} = \frac{\text{Volume of liquid in question}}{\text{Total volume of solution}} \times 100 \qquad (8.6)$$

3. **Mass by volume percentage (*m*/*V*):** This method expresses concentration as grams of solute per 100 mL of solution. With this system, a 10.0% *m*/*V* glucose solution is made by dissolving 10.0 g of glucose in water, diluting to 100 mL, and mixing. The 10.0% *m*/*V* solution could also be made by diluting 20.0 g to 200 mL, 50.0 g to 500 mL and so on. Of course, any other appropriate dilution ratio may be used:

$$\text{Mass by volume percent} = \frac{\text{g solute}}{\text{mL solution}} \times 100 \qquad (8.7)$$

4. **Parts per million/billion:** Percent by mass is equivalent to *parts per hundred*. When concentrations are very low, however, two closely related units become more convenient. These units are parts per million (ppm) and parts per billion (ppb). For example, the concentration of carbon dioxide in the atmosphere is currently 0.0380%. It is more conveniently represented as 380 ppm. Dioxin, a synthetic chemical linked to cancer, is measured in the soil in units of ppb.

   Parts per million is obtained by multiplying the ratio of the mass of solute to mass of solution by 10^6 ppm rather than 100%. Parts per billion is obtained by multiplying the same ratio by 10^9 ppb. For example, if a solution has a mass of 1 kg and contains only 3 mg of a solute, it has the following concentration in percent by mass, ppm and ppb.

$$\frac{3.0 \times 10^{-3}\,\text{g(solute)}}{1.0 \times 10^{3}\,\text{g(solution)}} \times 100\% = 3.0 \times 10^{-4}\%$$

$$\frac{3.0 \times 10^{-3}\,\text{g}}{1.0 \times 10^{3}\,\text{g}} \times 10^{6}\ \text{ppm} = 3.0\ \text{ppm}$$

$$\frac{3.0 \times 10^{-3}\,\text{g}}{1.0 \times 10^{3}\,\text{g}} \times 10^{9}\ \text{ppb} = 3.0 \times 10^{3}\,\text{ppb}$$

In this case, the most convenient expression of concentration is in units of ppm. (Caution: In the examples cited, the units, ppm and ppb, refer to the mass of the solution.) In the case of the concentration of CO_2 in the atmosphere, ppm refers to 1 million particles (molecules of compounds or atoms of noble gases) in the atmosphere. Thus, there are currently 380 CO_2 molecules per million molecules present in the atmosphere.

5. **Mole fraction:** The mole fraction x_A of a substance A is given by

$$x_\mathrm{A} = \frac{n_\mathrm{A}}{n_\mathrm{A} + n_\mathrm{B} + n_\mathrm{C} + n_\mathrm{D} + \cdots + n_\mathrm{Z}} \tag{8.8}$$

where n_A, n_B, n_C, …, n_Z are the numbers of moles of each component, A, B, C, …, Z, respectively. The sum of all mole fractions for a mixture must always be equal to 1. The mole percent is obtained by multiplying the mole fraction by 100%.

6. **Molarity:** We need a method of expressing concentration that will easily indicate how many moles of solute are present per unit volume of solution. For this purpose, the concentration known as molarity is used in calculations involving chemical reactions.

   A 1 molar solution contains 1 mol of solute per liter of solution. For example, to make a 1 molar solution of sodium hydroxide (NaOH) we dissolve 40 g NaOH (1 mol) in water and dilute the solution with more water to a volume of 1 L. The solution contains 1 mol of the solute in 1 L of solution and is said to be 1 molar in concentration.

   The concentration of a solution can, of course, be varied by using more or less solute or solvent; but in any case the **molarity** of a solution is the number of moles of solute per liter of solution. The abbreviation for molarity is M. The units of molarity are moles per liter (or mol L^{-1}).

$$\text{Molarity} = M = \frac{\text{Number of moles of solute}}{\text{Liter of solution}} = \frac{\text{Mole}}{\text{Liter}} \tag{8.9}$$

7. **Molality:** The ***molality* (*m*)** of a solution is the number of moles of solute per kilogram of solvent:

$$m = \frac{\text{Moles of solute}}{\text{Kilograms of solvent}} \tag{8.10}$$

   Note that a lower case *m* is used for molality concentrations and a capital *M* for molarity.

8. **Formality (*F*):** The number of gram formula weight of the substance dissolved per liter of the solution:

$$\text{Formality} = \frac{\text{Concentration of solute per liter of solution}}{\text{Formula weight}} \tag{8.11}$$

   Formality is generally used to express concentration of ionic compounds.

9. **Normality (*N*):** The number of gram-equivalent weight of the substance dissolved per liter of solution

$$\text{Normality} = \frac{\text{Concentration of solute per liter of solution}}{\text{Equivalent weight of solute}} \tag{8.12}$$

Note: It is important not to confuse *molarity* with *molality*.

$$\text{Molality} = m = \frac{\text{mol of solute}}{\text{kg of solvent}} \qquad \text{Molarity} = M = \frac{\text{mol of solute}}{\text{L of solution}}$$

The molarity of a solution changes slightly with temperature, but molality does not. Therefore, molality is more convenient in experiments involving temperature changes.

When water is the solvent, solution's molarity approaches to its molality as the solution becomes more dilute. In very dilute solutions, 1 L of *solution* is nearly 1 L of water, which has a mass close to 1 kg. Under these conditions, the ratio of moles per liter (molarity) is nearly the same as the ratio of moles per kilogram (molality). This only applies when the solvent is water.

For studying physical properties, however, molarity is not preferred because the molarity of a solution varies slightly with temperature. Most liquids expand slightly when heated, so a given solution will have a larger volume, and therefore a lower ratio of moles to volume, as its temperature is raised. For this reason, temperature-insensitive concentration units are used. The most common are *percentage by mass*, *molality*, and *mole fraction* (or *mole percent*).

Solved Example 8-14

Seawater is typically 3.5% sea salt and has a density of about 1.03 g mL^{-1}. How many grams of sea salt would be needed to prepare enough seawater solution to completely fill a 62.5 L aquarium?

Solution

Given that 3.5 g sea salt contains 100 g of solution

Therefore, 1.03 g solution contains 1.00 mL solution

Therefore, 62.5 L solution has

$$62.5\text{ L soln} \times \frac{1000\text{ mL soln}}{1\text{ L soln}} \times \frac{1.03\text{ g soln}}{1.00\text{ mL soln}} \times \frac{3.5\text{ g sea salt}}{100\text{ g soln}} = 2.2\times10^3\text{ g sea salt}$$

Solved Example 8-15

What volume of water at 20°C (density = 0.9982 g cm^{-3}) is needed to dissolve 45.0 g of sucrose to make a 10% (*w*/*w*) solution?

Solution

A 10% (*w*/*w*) solution of sucrose will need 10 g of sucrose for each 100 g of solution. For a solution with 45.0 g of sucrose:

$$10\%\text{ solution} = \frac{45.0\text{ g sucrose}}{x\text{ g solution}} \Rightarrow x = 450\text{ g solution}$$

Now, g water = 450 g solution – 45.0 g sucrose = 405 g water

So, mL water =

$$(405\text{ g water}) \times \left(\frac{1\text{ cm}^3}{0.9982\text{ g}}\right) = 405.7\text{ mL water}$$

Solved Example 8-16

How many grams of NaBr are needed to prepare 250 g of 1.00% (*w*/*w*) NaBr solution in water? How many grams of water are needed? How many milliliters are needed, given that the density of water at room temperature is 0.988 g mL^{-1}?

Solution

The total mass of the solution is to be 250 g. If the solution is to be 1.00% (*w*/*w*) NaBr, then the mass of NaBr will be: 250 g × 1.00 g NaBr/100 g solution = 2.50 g NaBr. We therefore need 2.50 g of NaBr and (250 – 2.50) = 248 g H_2O. The volume of water that is needed is: 248 g × 0.988 g mL^{-1} = 251 mL H_2O.

Solved Example 8-17

Hydrochloric acid can be purchased from chemical supply houses as a solution that is 37% (*w*/*w*) HCl. What mass of this solution contains 7.5 g of HCl?

Solution

An HCl solution that is 37% (*w*/*w*) has 37 g of HCl for every 1.0×10^2 g of solution.

$$\text{g solution} = (7.5\text{ g HCl})\left(\frac{1.0 \times 10^2\text{ g solution}}{37\text{ g HCl}}\right)$$

$$\times 2.0 \times 10^1\text{ g solution}$$

Solved Example 8-18

An experiment calls for a 0.150 molal solution of sodium chloride in water. How many grams of NaCl would have to be dissolved in 500.0 g of water to prepare a solution of this molality?

Solution

The concentration 0.150 molal means that the solution must contain 0.150 mol of NaCl for every 1.000 kg (1000 g) of water. So, we can write

0.150 mol of NaCl is dissolved in 1000 g H_2O

To calculate the number of moles of NaCl needed for 500.0 g of H_2O, we use this relationship as a conversion factor. We can then use the molar mass of NaCl to convert moles of NaCl into grams of NaCl.

$$500.0\text{ g } H_2O \times \frac{0.150\text{ mol NaCl}}{1000\text{ g } H_2O} \times \frac{58.44\text{ g NaCl}}{1\text{ mol NaCl}}$$

$$= 4.38\text{ g NaCl}$$

When 4.38 g of NaCl is dissolved in 500 g of H_2O, the concentration is 0.150 molal NaCl.

Solved Example 8-19

If you prepare a solution by dissolving 44.00 g of Na_2SO_4 in 250.0 g of water, what is the molality of the solution? Is the molarity of this solution numerically larger or smaller than its molality?

Solution

We need to know the number of moles of Na_2SO_4 and the number of kg of water.

44.00 g Na_2SO_4 ÷ 142.0 g mol^{-1} = 0.3099 mol NaOH
250 g H_2O × 1 kg/1000 g = 0.250 kg H_2O
The molality is thus given by:
m = 0.3099 mol/0.25 kg = 1.239 mol NaOH/kg H_2O = 1.239 molal

Solved Example 8-20

Calculate the number of grams of methanol (CH_3OH) needed to prepare a 0.250 molal solution, using 2.000 kg of water.

Solution

The number of grams of methanol (CH_3OH) needed

$$= (2000\text{ g } H_2O)$$

$$\times \left(\frac{0.250\text{ mol } CH_3OH}{1000\text{ g } H_2O}\right)\left(\frac{32.0\text{ g } CH_3OH}{1\text{ mol } CH_3OH}\right)$$

$$= 16.0\text{ g } CH_3OH$$

Solved Example 8-21

What mass of a 0.853 molal solution of $Fe(NO_3)_3$ is needed to obtain **(a)** 0.0200 mol of $Fe(NO_3)_3$, **(b)** 0.0500 mol of Fe^{3+} ions, and **(c)** 0.00300 mol of nitrate ions?

Solution

First we need to find the number of grams of $Fe(NO_3)_3$ for each kg of solvent.

$$0.853\text{ g Fe(NO}_3)_3 = 0.853\text{ mol Fe(NO}_3)_3 \times \left(\frac{241.86\text{ g Fe(NO}_3)_3}{1\text{ mol Fe(NO}_3)_3}\right) = 206.3\text{ g Fe(NO}_3)_3$$

Then we need to find how the ratio of the moles of $Fe(NO_3)_3$ to the mass of the solution:

$$\text{Ratio} = \frac{0.853\text{ mol Fe(NO}_3)_3}{1000\text{ g H}_2\text{O} + 206.3\text{ g Fe(NO}_3)_3}$$
$$= 7.072 \times 10^{-4}\text{ mol Fe(NO}_3)_3\text{ per g solution}$$

(a) Now, g solution = (0.0200 mol $Fe(NO_3)_3$) $\times$

$$\left(\frac{1\text{ g solvent}}{7.07 \times 10^{-4}\text{ mol Fe(NO}_3)_3}\right) = 28.3\text{ g solution}$$

(b) g solution = $(0.0500\text{ mol Fe}^{3+})\left(\frac{1\text{ mol Fe(NO}_3)_3}{1\text{ mol Fe}^{3+}}\right) \times$

$$\left(\frac{1\text{ g solvent}}{7.07 \times 10^{-4}\text{ mol Fe(NO}_3)_3}\right) = 70.7\text{ g solution}$$

(c) g solution = $(0.00300\text{ mol NO}_3^-)\left(\frac{1\text{ mol Fe(NO}_3)_3}{3\text{ mol NO}_3^-}\right) \times$

$$\left(\frac{1\text{ g solvent}}{7.07 \times 10^{-4}\text{ mol Fe(NO}_3)_3}\right) = 1.41\text{ g solution}$$

Solved Example 8-22

What will be the mole fraction of KI, if the density of 20% (mass/mass) aqueous KI is 1.202 g mL^{-1}?

Solution

Density of solution = mass/volume. Let the volume of solution is 1000 mL. Then

$$\text{Mass of solution} = \text{Density} \times \text{Volume}$$
$$= 1.202 \times 1000 = 1202\text{ g}$$

Now, 20% (*w*/*w*) KI means

$$\text{Mass of KI} = \frac{1202 \times 20}{100} = 240.4\text{ g}$$

$$\text{Therefore, mole fraction} = \frac{\dfrac{240.4}{166}}{\dfrac{240.4}{166} + \dfrac{961.6}{18}} = 0.0263$$

Conversions Among Concentration Units

There are times when we need to relate concentrations expressed in different units. **Molality** is a convenient method to express the concentration because it involves the mass of liquids rather than their volumes. It is also independent of the variation in temperature. The following expressions show the relation between several units.

1. **Relation between molality and molarity:**

   Molality (m) is defined as the number of moles of the solute per kilogram (kg) of the solvent and is expressed as

$$\text{Molality}\,(m) = \frac{\text{Moles of solute}}{\text{Mass of solvent in kg}} \qquad (8.13)$$

Molarity (M) is defined as number of moles of solute dissolved in 1 L of solution

$$\text{Molarity}\,(M) = \frac{\text{Moles of solute}}{\text{Volume of solution in liter}} \tag{8.14}$$

The density of a solution is defined as ratio of mass and volume. Mathematically it is written as

$$\text{Density}\ (\rho) = \frac{\text{Mass}}{\text{Volume}} \tag{8.15}$$

Solving Eqs. (8.13)–(8.15), we get the relation between molarity and molality as

$$\frac{\rho}{M} = \frac{1}{m} + \frac{M_{\text{solute}}}{1000}$$

where M_{solute} is the molecular mass of the solute.

2. **Relation between mole fraction and molality:**

$$x_A = \frac{n_A}{n_A + n_B} \quad \text{and} \quad x_B = \frac{n_B}{n_A + n_B}$$

$$\frac{x_A}{x_B} = \frac{n_A}{n_B} = \frac{\text{Moles of solute}}{\text{Moles of solvent}} = \frac{w_A \times M_B}{w_B \times M_A}$$

$$\frac{x_A \times 1000}{x_B \times M_B} = \frac{w_A \times 1000}{w_B \times M_A} = m \Rightarrow \frac{x_A \times 1000}{(1 - x_A)\,M_B} = m \tag{8.16}$$

3. **Relation between molality and solubility:**

$$\text{Molality} = \frac{\text{Solubility} \times 10}{\text{Molecular mass of the solute}} \tag{8.17}$$

$$\left[\text{Solubility} = \frac{\text{Mass of solute in gram}}{\text{Mass of solvent in gram}} \times 100\right]$$

4. **Relation between molarity and mole fraction:** Let M be the molarity of solution, and x_A and x_B be mole fractions of solvent and solute, respectively. When n_A and n_B moles of solvent and solute are mixed to form a solution, then mass of solution is $n_AM_A + n_BM_B$ where M_A and M_B are molar masses of solvent and solute, respectively. Then,

$$\text{Volume of solution} = \frac{\text{Mass}}{\text{Density}} = \frac{(n_A M_A + n_B M_B)}{\rho}$$

Now

$$\text{Molarity} = \text{Number of moles of solute} \times \frac{1000}{\text{Volume of solution}}$$

$$M = n_B \times \frac{1000 \times \rho}{(n_A M_A + n_B M_B)}$$

Dividing both numerator and denominator by $(n_A + n_B)$, we get

$$M = \frac{x_B \times 1000 \times \rho}{x_A M_A + x_B M_B} \tag{8.18}$$

5. **Relationship between molality and mole fraction:** Let m be the molality of solution, and x_A and x_B be mole fractions of solvent and solute, respectively. When n_A and n_B moles of solvent and solute are mixed to form a solution, then mass of solution is $n_A M_A + n_B M_B$ where M_A and M_B are molar masses of solvent and solute, respectively. Then,

$$\text{Molality} = \frac{\text{Number of moles of solute}}{\text{Mass of solvent}} \times 1000 \Rightarrow m = \frac{n_B}{n_A M_A} \times 1000$$

Dividing both numerator and denominator by $(n_A + n_B)$, we get

$$m = \frac{x_B}{x_A M_A} \times 1000 \tag{8.19}$$

6. **Relationship between normality and molarity:** We know that,

$$\text{Strength of the solution (g L}^{-1}) = \text{Molarity} \times \text{Molecular mass}$$

Also,

$$\text{Strength of the solution (g L}^{-1}) = \text{Normality} \times \text{Equivalent mass}$$

Equating both relations, we get

$$\text{Molarity} \times \text{Molecular mass} = \text{Normality} \times \text{Equivalent mass}$$

$$\frac{\text{Normality}}{\text{Molarity}} = \frac{\text{Molecular mass}}{\text{Equivalent mass}} = n$$

Therefore,

$$\text{Normality} = n \times \text{Molarity} \tag{8.20}$$

7. **Relationship between mass percent and molality:** Let m be the molality of solution, x be the mass percent of solute and M_B be the molecular weight of solute. Then,

Number of moles of solute = x/M_B mol
Mass of solvent = $(100 - x)$ g

$$\text{Molality} = \frac{\text{Number of moles of solute}}{\text{Mass of solvent}} \times 1000 \Rightarrow m = \frac{x/M_B}{100 - x} \times 1000 \tag{8.21}$$

8. **Relationship between mass percent and molarity:** Let m be the molality of solution, x be the mass percent of solute and M_B be the molecular weight of solute. Then,

Number of moles of solute = x/M_B
Volume of solution = Mass/Density = $100/\rho$

$$\text{Molarity} = \frac{\text{Number of moles of solute}}{\text{Volume of solution}} \times 1000 \Rightarrow M = \frac{x/M_B}{100/\rho} \times 1000 \tag{8.22}$$

Solved Example 8-23

What is the molality of 10.0% (w/w) aqueous NaCl?

Solution

We know that 58.44 g of NaCl is present in 1 mol of NaCl.

So, 10 g of NaCl is present in 10/58.44 mol of NaCl.

Given that 10 g of NaCl dissolves in 100 g of solution. So, mass of solute, that is, water = 100 – 10 = 90 g

Thus, molality can be calculated as

$$m = \frac{10/58.44}{90} \times 1000 = 1.90 \text{ molal}$$

Solved Example 8-24

A bottle on the shelf reads 50% sodium hydroxide solution. What is the molality of this solution?

Solution

If a solution is 50% NaOH, then it has 50 g of NaOH for each 100 g of solution. The mass of water is 50 g of water for 50 g of NaOH. To calculate the molality of the solution, we need to find the moles of NaOH for each kilogram of water.

$$m = \left(\frac{50 \text{ g NaOH}}{50 \text{ g H}_2\text{O}}\right)\left(\frac{1 \text{ mol NaOH}}{40.0 \text{ g NaOH}}\right)\left(\frac{1000 \text{ g H}_2\text{O}}{1 \text{ kg H}_2\text{O}}\right)$$

$$= 25 \text{ mol NaOH/kg H}_2\text{O} = 25 \text{ molal NaOH}$$

Solved Example 8-25

A certain sample of concentrated hydrochloric acid is 37.0% HCl. Calculate the molality of this solution.

Solution

If a solution is 37.0% (w/w) HCl, then 37.0% of the mass of any sample of such a solution is HCl and (100.0 – 37.0) = 63.0% of the mass is water. In order to determine the molality of the solution, we can conveniently choose 100.0 g of the solution as a starting point. Then 37.0 g of this solution are HCl and 63.0 g are H_2O.

For molality, we need to know the number of moles of HCl and the mass in kg of the solvent:

$$37.0 \text{ g HCl} \div 36.46 \text{ g mol}^{-1} = 1.01 \text{ mol HCl}$$
$$63.0 \text{ g H}_2\text{O} \times 1 \text{ kg}/1000 \text{ g} = 0.0630 \text{ kg H}_2\text{O}$$

Therefore,

$$\text{Molality} = \frac{\text{mol HCl}}{\text{kg H}_2\text{O}} = \frac{1.01 \text{ mol}}{0.0630 \text{ kg}} = 16.1 \text{ molal}$$

Solved Example 8-26

A certain supply of concentrated hydrochloric acid has a concentration of 36.0% HCl. The density of the solution is 1.19 g mL^{-1}. Calculate the molar concentration of HCl.

Solution

We know that 36.5 g of HCl is present in 1 mol of HCl.

So, 36 g of HCl is present in 36/36.5 mol of HCl.

Given that 36 g of NaCl dissolves in 100 g of solution. and density = 1.19 g mL^{-1}

Now, volume of solution = mass/density = 100/1.19

Thus, molarity can be calculated as

$$M = \frac{36/36.5}{100/1.19} \times 1000 = 11.7 \text{ M}$$

Note: The above two examples illustrated that when the concentration of an aqueous solution is very low, one gram per liter for example, the molality and the molarity are very close to the same numerical value. As a result we can conveniently interchange molality and molarity when aqueous solutions are very dilute.

Solved Example 8-27

Hydrobromic acid can be purchased as 40.0% HBr. The density of this solution is 1.38 g mL^{-1}. What is the molar concentration of HBr in this solution?

Solution

We first determine the mass of one L (1000 mL) of this solution, using the density:

$$1000\text{ mL} \times 1.38\text{ g mL}^{-1} = 1.38 \times 10^3\text{ g}$$

Next, we use the fact that 40.0% of this total mass is due to HBr, and calculate the mass of HBr in the 1000 mL of solution:

$$0.400 \times (1.38 \times 10^3) = 552\text{ g HBr}$$

This is converted to the number of moles of HBr in 552 g as 552 g HBr ÷ 80.91 g mol^{-1} = 6.82 mol HBr

Last, the molarity is the number of moles of HBr per liter of solution = 6.82 mol/1 L = 6.82 M

Solved Example 8-28

One gram of $Al(NO_3)_3$ is dissolved in 1.00 L of water at 20°C. The density of water at this temperature is 0.9982 g cm^{-3} and the density of the resulting solution is 0.9989 g cm^{-3}. Calculate the molarity and molality of this solution. (Hint: remember that density can be used to convert mass to volume.)

Solution

First determine the number of moles of $Al(NO_3)_3$ dissolved in the liter of water.

$$\text{mol Al(NO}_3)_3 = (1.00\text{ g Al(NO}_3)_3)\left(\frac{1\text{ mol Al(NO}_3)_3}{212.996\text{ g Al(NO}_3)_3}\right)$$

$$= 0.00469\text{ mol Al(NO}_3)_3$$

Next find the mass of the water:

$$\text{g H}_2\text{O} = (1.00\text{ L H}_2\text{O})\left(\frac{1000\text{ mL H}_2\text{O}}{1\text{ L H}_2\text{O}}\right)\left(\frac{0.9982\text{ g H}_2\text{O}}{1\text{ mL H}_2\text{O}}\right)$$

$$= 998.2\text{ g H}_2\text{O}$$

To find the molarity of the solution, first we need to find the mass of the solution, and then the volume of the solution:

$$\text{g solution} = 998.2\text{ g H}_2\text{O} + 1.00\text{ g Al(NO}_3)_3$$

$$= 999.2\text{ g solution}$$

$$\text{L solution} = (999.2\text{ solution}) \times$$

$$\left(\frac{1\text{ mL solution}}{0.9989\text{ g solution}}\right)\left(\frac{1\text{ L solution}}{1000\text{ mL solution}}\right) = 1.0003\text{ L}$$

$$M\text{ of solution} = \frac{0.00469\text{ mol Al(NO}_3)_3}{1.0003\text{ L solution}}$$

$$= 0.00469\text{ M Al(NO}_3)_3$$

The molality of the solution can also be determined

$$m\text{ of solution} = \frac{0.00469\text{ mol Al(NO}_3)_3}{0.9982\text{ kg H}_2\text{O}}$$

$$= 0.00470\text{ molal Al(NO}_3)_3$$

Solved Example 8-29

The density of 1.45 molal solution of acetic acid is 1.012 g cm^{-3}. Calculate its molarity.

Solution

Molarity and molaity are related as $M = \dfrac{m\rho}{1 + mM_B}$. So, we have

$$M = \frac{m\rho}{1 + mM_B} = \frac{(1.450\text{ mol kg}^{-1})(1.012\text{ g cm}^{-3})}{1 + (1.450\text{ mol kg}^{-1})(60\text{ g mol}^{-1})}$$

$$\frac{(1.45\text{ mol kg}^{-1})[1.012(10^{-3}\text{ kg})(10^{-1}\text{ dm})^3]}{1 + (1.45\text{ mol kg}^{-1})[60(10^{-3}\text{ kg})\text{ mol}^{-1}]}$$

$$= \frac{1.450 \times 1.012}{1 + 1.450 \times 60 \times 10^{-3}}\text{ mol dm}^{-3}$$

$$= 1.35\text{ mol dm}^{-3}$$

Solved Example 8-30

The mole fraction of methanol in aqueous solution is 0.02. Calculate the molality of the solution.

Solution

Let the number moles of methanol = n_B and its molar mass be M_B.

The number moles of the water be n_A and its molar mass is 18. Then the mass of water = $18n_A$. Hence, molality becomes

$$m = \frac{n_B}{n_A M_A} \times 1000$$

Dividing numerator and denominator by $n_A + n_B$, we get

$$m = \frac{x_B}{x_A M_A} \times 1000 = \frac{0.02 \times 1000}{(1-0.02)\times 18}$$
$$= \frac{0.02 \times 1000}{0.98 \times 18} = 1.134 \text{ molal}$$

8.7 | VAPOR PRESSURE OF SOLUTIONS

All solutions in which the solvent is a liquid are called **liquid solutions**. The solute may be a gas, liquid or solid. We have seen that the properties of a solution of gas in a liquid are governed by Henry's law. In this section, we will study the properties of solid or liquid solute in a liquid solution. The liquid solvent is generally volatile whereas the solute may be volatile or non-volatile. Though a solution may have more than one solute, we will restrict our discussion to binary solutions that is where total number of components is two, that is, (a) liquid in liquid and (b) solid in liquid.

Note: Vapor pressure is the pressure of the vapor resulting from evaporation of a liquid (or solid) in a closed system.

Raoult's Law

Raoult's law states that for a solution containing a non-volatile solute, the vapor pressure of the solution is directly proportional to mole fraction of the solvent.

$$p_{\text{solution}} = \underset{\text{constant}}{\underset{\downarrow}{K}} \; (x_{\text{solvent}}) \tag{8.23}$$

Now if $x_{\text{solvent}} = 1$, then $p_{\text{solution}} = p_{\text{solvent}}$ = vapor pressure of pure solvent. Therefore,

$$p^{\circ}_{\text{solvent}} = K(1) \tag{8.24}$$

Then substituting Eq. (8.24) in Eq. (8.23), we get

$$p_{\text{solution}} = p^{\circ}_{\text{solvent}} \cdot x_{\text{solvent}}$$

Vapor Pressure of Liquid–Liquid Solutions

When two (or more) components of a liquid solution can evaporate, the vapor contains molecules of each substance. Each volatile component contributes its own partial pressure to the total pressure. Consider a binary solution of two components A and B (both liquids). Let p total be the total vapor pressure of the solution due to both the components and let p_A and p_B be the partial pressures of component A and B, respectively. Then by Raoult's law, the partial pressure of a particular component is directly proportional to the component's mole fraction in the solution. By Dalton's law of partial pressures, the total vapor pressure will be the sum of the partial pressures. To calculate these partial pressures, we use the **Raoult's law equation** for each component. When component A is present in a mole fraction of x_A, its partial pressure (p_A) is this fraction of its vapor pressure when pure, namely, p°_A.

$$p_A = x_A p^{\circ}_A \tag{8.25}$$

And, by the same argument, p_B, the partial pressure of component B, is

$$p_B = x_B p_B^{\circ} \tag{8.26}$$

The total vapor pressure of the solution of liquids A and B is then, by Dalton's law of partial pressures, the sum of p_A and p_B.

$$p_{\text{total}} = p_A + p_B$$

Substituting for p_A and p_B, we get

$$p_{\text{total}} = x_A p_A^{\circ} + x_B p_B^{\circ} \tag{8.27}$$

Notice that this equation contains the Raoult's law equation as a special case. If one component, say, component B, is non-volatile, it has no vapor pressure (p_B° is zero) so the $x_B p_B^{\circ}$ term drops out, leaving the Raoult's law equation. Further, the total vapor pressure of the solution in which both the components are volatile can be related to the mole fraction of any one component using the relation $x_A + x_B = 1$ or $x_A = 1 - x_B$ in Eq. (8.27). Then

$$p_{\text{total}} = (1 - x_B)p_A^{\circ} + x_B p_B^{\circ} = p_A^{\circ} + (p_B^{\circ} - p_A^{\circ})x_B \tag{8.28}$$

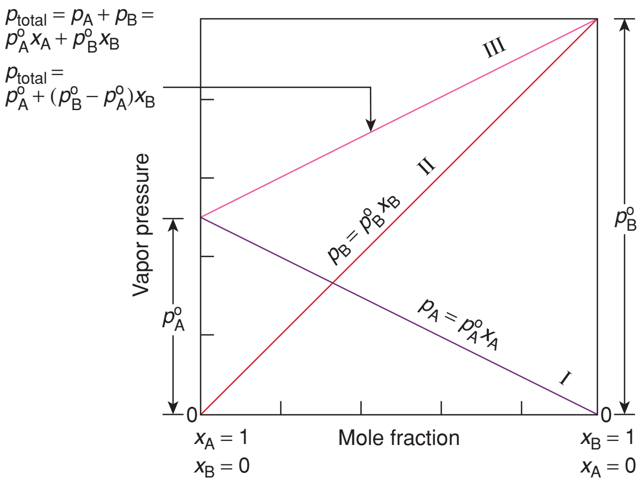


Figure 8.8 Change of vapor pressure with the mole fraction for an ideal solution.

The equation shows that vapor pressure of the solution is a linear function of mole fraction of either of the components, and it can also be related to mole fraction of any one component. A plot of vapor pressure vs. mole fractions of a binary solution is shown in Fig. 8.8.

From the plot, we can see that

1. When only component A is present, that is $x_A = 1$ and $x_B = 0$, the vapor pressure corresponds to that of pure component A. As component B is added, the mole fraction of A decreases and so does the vapor pressure, as shown along line I.
2. When only pure component B is present, that is $x_A = 0$ and $x_B = 1$, the vapor pressure corresponds to that of pure component B. As component A is added, the mole fraction of B decreases and so does its vapor pressure, as shown along line II.
3. Depending on the vapor pressure of pure components A and B, the total vapor pressure over the binary solution varies between the vapor pressure of A and B as shown along line III.
4. If component A is less volatile than component B, that is $p_A^{\circ} < p_B^{\circ}$, then from the graph we can see that the maximum value of p_{total} is p_B° and the minimum value is p_A°.

The vapor phase over the solution is in equilibrium with the solution and its composition can be determined by the partial pressures p_A and p_B of the components A and B. If y_A and y_B are the mole fractions of A and B, respectively, in the vapor phase, then by Dalton's law

$$p_A = y_A p_{\text{total}}$$

and

$$p_B = y_B p_{\text{total}}$$

Solved Example 8-31

Acetone (molar mass 58.1 g mol^{-1}) has a vapor pressure at a given temperature of 162 mm Hg. How many grams of the non-volatile stearic acid (molar mass 284.5 g mol^{-1}) must be added to 156 g of acetone to decrease its vapor pressure to 150 mm Hg?

Solution

We know that $p_{\text{acetone}} = x_{\text{acetone}} \times p^{\text{o}}_{\text{acetone}}$. First, solve for the mole fraction of acetone:

$$150 \text{ mm Hg} = x_{\text{acetone}} \times 162 \text{ mm Hg} \Rightarrow x_{\text{acetone}} = 0.926$$

Now solve for the moles of steric acid:

$$x_{\text{acetone}} = \frac{\text{mol acetone}}{\text{mol acetone} + \text{mol stearic acid}}$$

$$\text{Mol acetone} = (156 \text{ g acetone})\left(\frac{1 \text{ mol acetone}}{58.0 \text{ mol acetone}}\right)$$

$$= 2.69 \text{ mol acetone}$$

$$x_{\text{acetone}} = 0.926 = \frac{2.69 \text{ mol acetone}}{2.69 \text{ mol acetone} + x \text{ mol stearic acid}}$$

(0.926)(2.69 mol acetone + x mol stearic acid) = 2.69 mol acetone

2.49 mol acetone + 0.926x mol stearic acid = 2.69 mol acetone

0.926x mol stearic acid = 0.199

x mol stearic acid = 0.215 mol stearic acid

Finally, solve to find the number of grams of stearic acid

$$\text{g stearic acid} = (0.215 \text{ mol stearic acid}) \times \left(\frac{284.5 \text{ g stearic acid}}{1 \text{ mol stearic acid}}\right) = 61.2 \text{ g stearic acid}$$

Solved Example 8-32

Acetone is a solvent for both water and molecular liquids that do not dissolve in water like benzene. At 20°C, acetone has a vapor pressure of 162 mm Hg and water has vapor pressure of 17.5 mm Hg. Assuming that the mixture obeys Raoult's law, what would be the vapor pressure of a solution of acetone and water with 50.0 mol% of each?

Solution

A concentration of 50 mol% corresponds to a mole fraction of 0.5, so

$$\begin{aligned} p_{\text{acetone}} &= 0.500 \times 162 \text{ mm Hg} = 81.0 \text{ mm Hg} \\ p_{\text{water}} &= 0.500 \times 17.5 \text{ mm Hg} = 8.75 \text{ mm Hg} \\ p_{\text{total}} &= 81.0 + 8.75 = 89.8 \text{ mm Hg} \end{aligned}$$

Solved Example 8-33

Two liquids A and B form ideal solutions. At 300K, the vapor pressure of a solution containing 1 mole of A and 3 moles of B is 550 mm of Hg. At the same temperature, if one more mole of B is added to this solution, the vapor pressure of the solution increases by 10 mm of Hg. Determine the vapor pressure of A and B in their pure state.

Solution

Let the vapor pressure of pure A be = p^{o}_{A} and the vapor pressure of pure B be = p^{o}_{B}. The total vapor pressure of solution (1 mole fraction of A and 3 is mole fraction of B). Therefore, we have the total vapor pressure as

$$550 = \frac{1}{4} p^{\text{o}}_{\text{A}} + \frac{3}{4} p^{\text{o}}_{\text{B}}$$

or

$$2200 = p^{\text{o}}_{\text{A}} + 3p^{\text{o}}_{\text{B}} \qquad (1)$$

The total vapor pressure of solution (when 1 mol A + 4 mol B) is

$$560 = \frac{1}{5} p^{\text{o}}_{\text{A}} + \frac{4}{5} p^{\text{o}}_{\text{B}}$$

or

$$2500 = p^{\text{o}}_{\text{A}} + 4p^{\text{o}}_{\text{B}} \qquad (2)$$

Solving Eqs. (1) and (2), we get $p^{\text{o}}_{\text{A}} = 400$ mm Hg and $p^{\text{o}}_{\text{B}} =$ 600 mm of Hg.

Vapor Pressure of Solutions of Solids in Liquids

The other class of liquid solutions consists of solids (non-volatile solute) dissolved in a liquid, for example, salt or sugar dissolved in water, sulphur dissolved in carbon disulphide, etc. All liquid solutions of **non-volatile** solutes (solutes that have no tendency to evaporate) have lower vapor pressures than their pure solvents. The vapor pressure of such a solution is proportional to how much of the solution actually consists of the solvent. This proportionality is given by **Raoult's law** (also known as the **vapor pressure–concentration law**) which says that the vapor pressure of the solution,

p_{solution}, equals the mole fraction of the solvent, x_{solvent}, multiplied by its vapor pressure when pure, that is, $p^{\circ}_{\text{solvent}}$. In equation form, Raoult's law is expressed as follows.

$$p_{\text{solution}} = x_{\text{solvent}}\, p^{\circ}_{\text{solvent}} \tag{8.29}$$

Because of the form of this equation, a plot of p_{solution} vs. x_{solvent} should be *linear* at all concentrations when the system obeys Raoult's law (see Fig. 8.9).

Notice that the mole fraction in Raoult's law refers to the solvent, not the solute. Usually, we are more interested in the effect of the *solute's* mole fraction concentration, x_{solute}, on the vapor pressure. We can show that the change in vapor pressure, Δp, is directly proportional to the mole fraction of solute, x_{solute}, as follows.

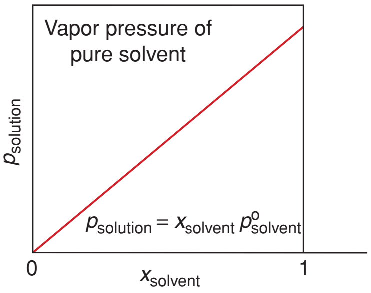


Figure 8.9 Raoult's law plot.

$$\Delta p = x_{\text{solute}}\, p^{\circ}_{\text{solvent}} \tag{8.30}$$

Here,
$$\Delta p = p^{\circ}_{\text{solvent}} - p_{\text{solution}}$$

So,
$$x_{\text{solute}} = \frac{(p^{\circ}_{\text{solvent}} - p_{\text{solution}})}{p^{\circ}_{\text{solvent}}}$$

This relation shows that relative lowering of vapor pressure x_{solute}. The change in vapor pressure equals the mole fraction of the solute times the solvent's vapor pressure when pure. The effect is shown in Fig. 8.10.

1. Figure 8.10(a) shows that an equilibrium between a pure solvent and its vapor. With a high number of solvent molecules in the liquid phase, the rates of evaporation and condensation are relatively high.
2. Figure 8.10(b) shows that in the solution, some of the solvent molecules have been replaced with solute molecules. There are fewer solvent molecules available to evaporate from solution. The evaporation rate is lower. When equilibrium is established, there are fewer solvent molecules in the vapor. The vapor pressure of the solution is less than that of the pure solvent.

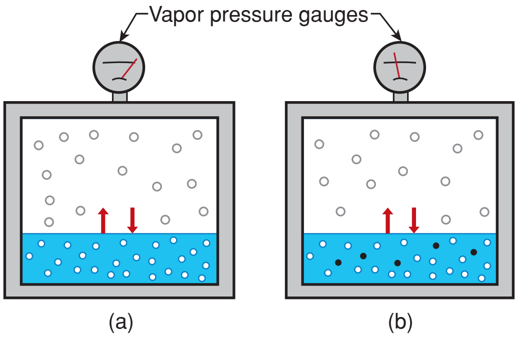


Figure 8.10 Effect of a non-volatile solute on the vapor pressure of a solvent.

Solved Example 8-34

Carbon tetrachloride has a vapor pressure of 100 mm Hg at 23°C. This solvent can dissolve candle wax, which is essentially non-volatile. Although candle wax is a mixture, we can take its molecular formula to be $C_{22}H_{46}$ (molar mass 311 g mol^{-1}). What is the vapor pressure at 23°C of a solution prepared by dissolving 10.0 g of wax in 40.0 g of CCl_4 (molar mass 154 g mol^{-1})?

Solution

First we calculate the moles of each component.

$$\text{For } CCl_4,\ 40.0\text{ g } CCl_4 \times \frac{1\text{ mol } CCl_4}{154\text{ g } CCl_4} = 0.260\text{ mol } CCl_4$$

For $C_{22}H_{46}$,

$$10.0\text{ g } C_{22}H_{46} \times \frac{1\text{ mol } C_{22}H_{46}}{311\text{ g } C_{22}H_{46}} = 0.0322\text{ mol } C_{22}H_{46}$$

$$\text{The total number of moles} = 0.292\text{ mol}$$

Now, we can calculate the mole fraction of the solute, $C_{22}H_{46}$.

$$x_{C_{22}H_{46}} = \frac{0.0322\text{ mol}}{0.292\text{ mol}} = 0.110$$

The amount that the vapor pressure is lowered, Δp, will be this particular mole fraction, 0.110, times the vapor pressure of pure CCl_4 (100 mm Hg), calculated by equation $\Delta p = x_{\text{solute}} \times p^{\circ}_{\text{solvent}}$

$$\Delta p = 0.110 \times 100\text{ mm Hg} = 11.0\text{ mm Hg}$$

The presence of the wax in the CCl_4 lowers the vapor pressure of the CCl_4 by 11.0 mm Hg (i.e., from 100 to 89 mm Hg).

8.8 | ENTHALPY OF SOLUTION

Because intermolecular attractive forces are important when liquids and solids are involved, the formation of a solution is inevitably associated with energy exchanges. The total energy absorbed or released when a solute dissolves in a solvent at constant pressure to make a solution is called the molar enthalpy of solution, or usually just the heat of solution, ΔH_{soln}.

1. **Solid in Liquid solution:** The molar enthalpy of solution of a solid in a liquid, also called the heat of solution, is the sum of the lattice energy and the solvation energy (or, when water is the solvent, the hydration energy). The lattice energy is the increase in the potential energy of the system required to separate the molecules or ions of the solute from each other. The solvation energy corresponds to the potential energy lowering that occurs in the system from the subsequent attractions of those particles to the solvent molecules as intermingling occurs.

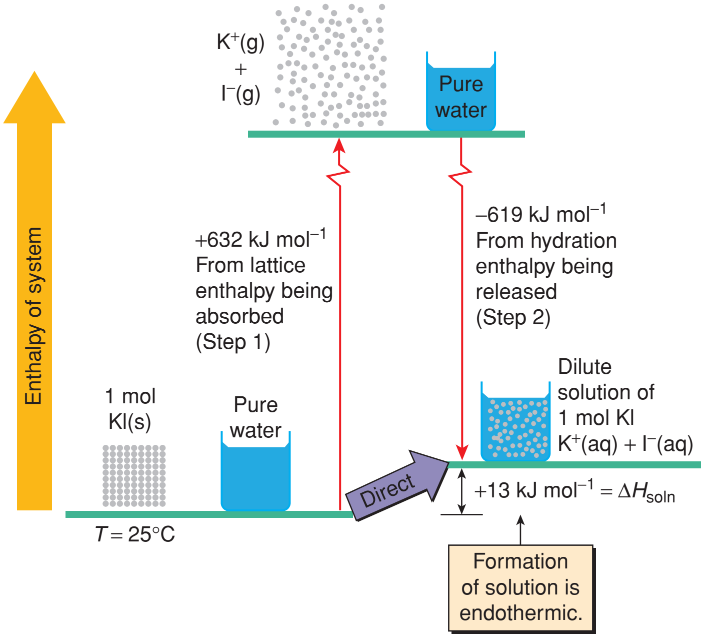
   Consider the enthalpy diagram showing these steps for potassium iodide is given in Fig. 8.11.

   Step 1: This corresponds to the lattice energy of KI, which is represented by the thermochemical equation

   $$\text{KI(s)} \rightarrow \text{K}^+\text{(g)} + \text{I}^-\text{(g)} \quad \Delta H = +632 \text{ kJ}$$

   Step 2: This corresponds to the hydration energy of gaseous K^+ and I^- ions.

   $$\text{K}^+\text{(g)} + \text{I}^-\text{(g)} \rightarrow \text{K}^+\text{(aq)} + \text{I}^-\text{(aq)} \quad \Delta H = -619 \text{ kJ}$$



Lattice energy:	$\text{KI(s)} \rightarrow \text{K}^+\text{(g)} + \text{I}^-\text{(g)}$	$\Delta H = +632 \text{ kJ}$
Hydration energy:	$\text{K}^+\text{(g)} + \text{I}^-\text{(g)} \rightarrow \text{K}^+\text{(aq)} + \text{I}^-\text{(aq)}$	$\Delta H = -619 \text{ kJ}$
Total:	$\text{KI(s)} \rightarrow \text{K}^+\text{(aq)} + \text{I}^-\text{(aq)}$	$\Delta H_{\text{soln}} = +13 \text{ kJ}$

Figure 8.11 Enthalpy diagram for the heat of solution of one mole of potassium iodide.

The *enthalpy of solution* is obtained from the sum of the equations for Steps 1 and 2 and is the enthalpy change when one mole of crystalline KI dissolves in water.

$$\text{KI(s)} \rightarrow \text{K}^+\text{(aq)} + \text{I}^-\text{(aq)} \quad \Delta H_{\text{soln}} = +13 \text{kJ}$$

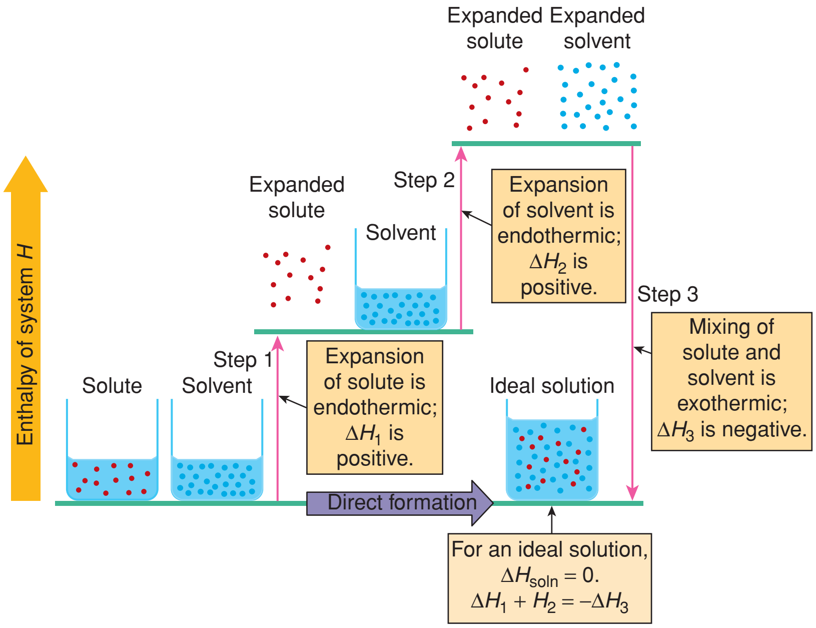
The positive value of ΔH_{soln} indicates that the solution process is endothermic for KI, in agreement with the observation that when KI is added to water and the mixture is stirred, it becomes cool as the KI dissolves.

2. **Liquid in liquid solution:** When liquids dissolve in liquids, an ideal solution forms if the potential energy increase needed to separate the molecules equals the energy lowering as the separated molecules come together. Usually, some net energy exchange occurs, however, and few solutions are ideal.

Imagine a three-step path going from the initial to the final state (see Fig. 8.12). We will designate one liquid as the solute and the other as the solvent. The steps involved are as follows:

Step 1: Expand the solute liquid. First, we imagine that the molecules of one liquid are moved apart just far enough to make room for molecules of the other liquid. Because we have to overcome forces of attraction, this step increases the system's potential energy and so is *endothermic*.

Step 2: Expand the solvent liquid. The second step is like the first, but is done to the other liquid (solvent). On an enthalpy diagram (Fig. 8.12) we have climbed two energy steps and have both the solvent and the solute in their slightly "expanded" conditions.



Expanded solute
Expanded solvent
Expanded solute
Step 2
Solvent
Expansion of solvent is endothermic; ΔH_2 is positive.
Step 3
Mixing of solute and solvent is exothermic; ΔH_3 is negative.
Enthalpy of system H
Step 1
Solute
Solvent
Expansion of solute is endothermic; ΔH_1 is positive.
Ideal solution
Direct formation
For an ideal solution, $\Delta H_{soln} = 0$. $\Delta H_1 + H_2 = -\Delta H_3$

Figure 8.12 Enthalpy changes in the formation of an ideal solution.

Step 3: Mix the expanded liquids. The third step brings the molecules of the expanded solvent and solute together to form the solution. Because the molecules of the two liquids experience mutual forces of attraction, bringing them together lowers the system's potential energy, so Step 3 is exothermic. The value of ΔH_{soln} will, again, be the net energy change for these steps.

The enthalpy diagram in Fig. 8.12 shows the case when the sum of the energy inputs for Steps 1 and 2 is equal to the energy released in Step 3, so the overall value of ΔH_{soln} is zero. For example, when we make a solution of benzene and carbon tetrachloride, the attractive forces between molecules of benzene are almost exactly the same as those between molecules of CCl_4, or between molecules of benzene and those of CCl_4. If all such intermolecular forces were identical, the net ΔH_{soln} would be exactly zero, and the resulting solution would be called an ideal solution.

Note: Be sure to notice the difference between an *ideal solution* and an *ideal gas*. In an ideal gas, there are no attractive forces. In an ideal solution, there are attractive forces, but they all have the same magnitude.

For most liquids that are mutually soluble, ΔH_{soln} is not zero. Instead, heat is either given off or absorbed. For example, acetone and water are liquids that form a solution exothermically (ΔH_{soln} is negative). With these liquids, the third step releases more energy than the sum of the first two chiefly because molecules of water and acetone attract each other more strongly than acetone molecules attract each other. This is because water molecules can form hydrogen bonds to acetone molecules in the solution, but acetone molecules cannot form hydrogen bonds to other acetone molecules in the pure liquid.

Ethanol (CH_3CH_2OH) and hexane ($CH_3CH_2CH_2CH_2CH_2CH_3$) form a solution endothermically. In this case, the release of energy in the third step is not enough to compensate for the energy demands of Steps 1 and 2, and the solution cools as it forms. Ethanol molecules attract each other more strongly than they can attract hexane molecules. Hexane molecules cannot push their way into ethanol without breaking up some of the hydrogen bonding between ethanol molecules.

3. **Solution of gas in gas:** Unlike the case for solid and liquid solutes, only very weak attractions exist between gas molecules, so the energy required to "expand the solute" is negligible. Since the gases are already separated and remain so gas mixture, the net enthalpy of solution is very small if not zero. The heat absorbed or released when a gas dissolves in a liquid has essentially two contributions, as shown in Fig. 8.13.

(a) Energy is absorbed to open "pockets" in the solvent that can hold gas molecules. The solvent must be expanded slightly to accommodate the molecules of the gas. This requires a small energy input since attractions between solvent molecules must be overcome. Water is a special case; it already contains open holes in its network of loose hydrogen bonds around room temperature. For water, very little energy is required to create pockets that can hold gas molecules.

(b) Energy is released when gas molecules enter the pockets. Intermolecular attractions between the gas molecules and the surrounding solvent molecules lower the total energy, and energy is released as heat. The stronger the attractions are, the more heat is released. Water is capable of forming hydrogen bonds with some gases, while organic solvents often can't. A larger amount of heat is released when a gas molecule is placed in the pocket in water than in organic solvents.

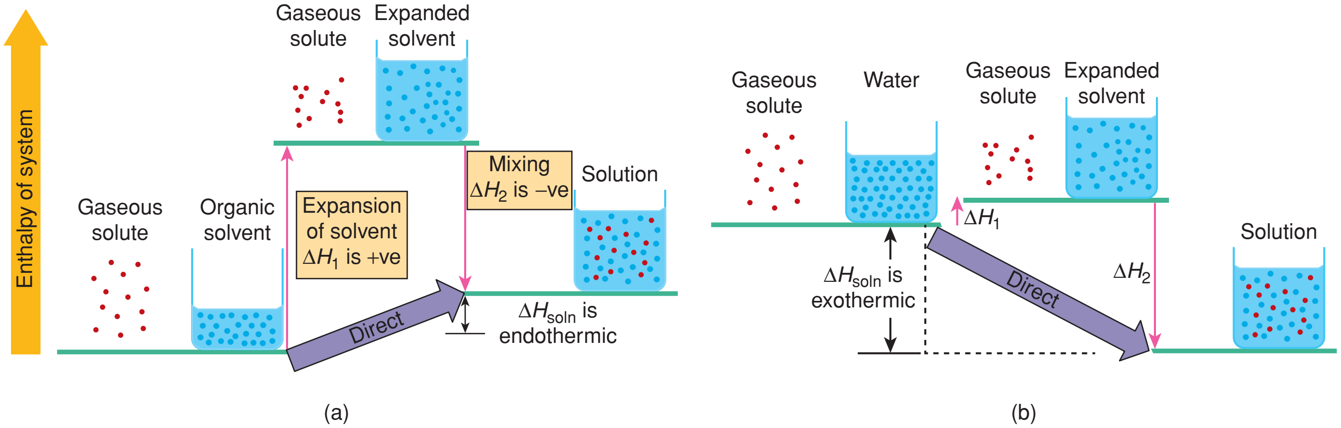


Figure 8.13 A molecular model of gas solubility.

These factors lead to two generalizations:

(a) When a gas dissolves in an organic solvent, the solution process is often endothermic because the energy required to open up pockets is greater than the energy released by attractions formed between the gas and solvent molecules.

(b) When a gas dissolves in water, the solution process is often exothermic because water already contains pockets to hold the gas molecules, and energy is released when water and gas molecules attract each other.

Solved Example 8-35

Suggest a reason why the value of ΔH_{soln} for a gas such as CO_2, dissolving in water, is negative.

Solution

When a gas dissolves in a liquid, there is no endothermic step analogous to the lattice energy of a solid. The only enthalpy change is the one associated with hydration, and this is always negative.

Solved Example 8-36

When a certain solid dissolves in water, the solution becomes cool. Is ΔH_{soln} for this solute positive or negative? Explain your reasoning. Is the solubility of this substance likely to increase or decrease with increasing temperature? Explain your answer using Le Chatelier's principle.

Solution

If the solution becomes cool, it is an endothermic process and the ΔH_{soln} is positive. This is because the solution is absorbing heat from the surroundings. The solubility is likely to increase with increasing temperature because heat is required for the reaction to proceed, so increasing the temperature increases the amount of heat available.

8.9 | IDEAL SOLUTIONS

The liquid–liquid solutions can be divided into ideal or non-ideal (real) based on whether they obey Raoult's law exactly or not. These differences between ideal and real solution behaviors are quite useful. They can tell us whether the attractive forces in the pure solvents, before mixing, are stronger or weaker than the attractive forces in the mixture.

A solution is said to be ideal if each of its components obeys Raoult's law for the entire composition range. In a binary solution of components A and B, the enthalpy of mixing ΔH_{mix} is zero, that is, in preparation of an ideal solution no thermal change is observed. This can be explained on the basis of interactive forces between A–A, B–B and A–B. If the interactive forces are of the same order, then the energy required to dissociate a molecule of A from component A or molecule of B from component B will be compensated by the energy released by association of A with B or B with A. For example, in the solution of benzene in CCl_4, attractive forces between molecules of benzene are almost exactly the same as those between molecules of CCl_4, or between molecules of benzene and those of CCl_4. If all such intermolecular forces were identical, the net ΔH_{soln} would be exactly zero, and the resulting solution would be called an **ideal solution**.

Mathematical proof: The above observation can be supported with mathematical proof as follows. Consider a homogeneous solution placed in a closed evacuated vessel. The total vapor pressure after it attained equilibrium is equal to the sum of partial pressure of its constituents. An ideal solution is the one which follows Raoult's law under all conditions of compositions.
The various constituents of an ideal solution will obey the following relationship:

$$\mu_i(\text{soln}) = \mu^{\text{o}}_{i(\text{l})} + RT\ln x_i$$

where $\mu_i(\text{soln})$ = chemical potential of ith constituent of the solution, $\mu_i^{\text{o}}(\text{l})$ = chemical potential of pure liquid constituent i and x_i = mole fraction of the constituent in the solution.

Hence,
$$\Delta G_{\text{mix}} = n_{\text{total}}\, RT\sum_i x_i \ln x_i$$
$$\Delta S_{\text{mix}} = -n_{\text{total}}\, RT\sum_i x_i \ln x_i$$

Now,
$$\Delta G = \Delta H - T\Delta S$$

Therefore, $\Delta H_{\text{mix}} = 0$. Hence, in the formation of an ideal solution neither heat is absorbed nor evolved, that is, heat change is zero.

In an ideal solution, the volume of mixing (ΔV_{mix}) is also zero, that is, the final volume of the solution is equal to the sum of volumes of components being mixed. Only a few pairs of liquid show ideal behavior, examples include, benzene and toluene, bromoethane and chloroethane, etc. However, all solutions when diluted approach ideal behavior.

Now, since $\Delta H_{\text{mix}} = 0$ and $\Delta V_{\text{mix}} = 0$ for an ideal solution, therefore we can conclude that the attractive force acting between the molecules of its constituents must be identical in nature, that is, A–A attractive force = B–B = A–B attractive forces.

Also the partial molar volume of a constituent in an ideal solution is equal to the molar volume of the constituent when present in the pure form. Some examples of ideal binary liquid solutions are as follows:

1. Ethylene dibromide and propylene dibromide at 358 K.
2. *n*-Hexane and *n*-heptane at 303 K.
3. Ethyl bromide and ethyl iodide at 303 K.
4. *n*-Butyl chloride and *n*-butyl bromide at 323 K.

Vapor Pressure of Ideal Binary Liquid Solution

Assuming both constituents (A and B) to form an ideal binary solution, following Raoult's law over the entire range of composition, the partial pressures exerted by vapors of their constituents over the solution, will be given by

$$p_{\text{A}} = p^{\text{o}}_{\text{A}} \cdot x_{\text{A}}$$
$$p_{\text{B}} = p^{\text{o}}_{\text{B}} \cdot x_{\text{B}}$$

where $x_{\text{A}}, x_{\text{B}}$ = mole fractions and $p^{\text{o}}_{\text{A}}, p^{\text{o}}_{\text{B}}$ = vapor pressure of pure constituents. Now,

$$p_{\text{T}} = p_{\text{A}} + p_{\text{B}} = x_{\text{A}} \cdot p^{\text{o}}_{\text{A}} + x_{\text{B}} \cdot p^{\text{o}}_{\text{B}}$$

Also, $x_A + x_B = 1$, thus we have

$$p_T = x_A \cdot p_A^o + (1 - x_A) p_B^o$$

$$p_T = p_B^o + (p_A^o - p_B^o) x_A$$

$$y = c + m \cdot x \qquad \text{(can be compared to equation of straight line)}$$

Further, the composition of the vapor phase can also be determined using Dalton's law.

$$y_A = \frac{p_A}{p_T} = \frac{p_A^o x_A}{p_B^o + (p_A^o - p_B^o) x_A}$$

$$y_B = \frac{p_B}{p_T} = 1 - y_A = \frac{x_B p_B^o}{p_A^o + (p_B^o - p_A^o) x_B}$$

$$x_A = \frac{y_A p_B^o}{p_A^o + (p_B^o - p_A^o) y_A}$$

$$p_T = p_B^o + (p_A^o - p_B^o) x_A = p_B^o + (p_A^o - p_B^o) \frac{y_A p_B^o}{p_A^o + (p_B^o - p_A^o) y_A}$$

Therefore,

$$p_T = \frac{p_B^o p_A^o}{p_A^o + (p_B^o - p_A^o) y_A}$$

or

$$\frac{1}{p_T} = \frac{p_A^o + (p_B^o - p_A^o) y_A}{p_B^o p_A^o} = \frac{1}{p_B^o} + \left(\frac{1}{p_A^o} - \frac{1}{p_B^o} \right) y_A$$

Solved Example 8-37

If the value of ΔH_{soln} for the formation of a mixture of two liquids A and B is zero, what does this imply about the relative strengths of A–A, B–B, and A–B intermolecular attractions?

Solution

The fact that the ΔH_{soln} value for the formation of a mixture of A and B is zero, implies that the relative strengths of A–A, B–B, and A–B intermolecular attractions are similar.

Solved Example 8-38

The molar volume of liquid benzene (density = 0.877 g mL^{-1}) increases by a factor of 2750 as it vaporizes at 20°C and that of liquid toluene (density = 0.867 g mL^{-1}) increases by a factor of 7720 at 20°C. A solution of benzene and toluene at 20°C has a vapor pressure of 46.0 torr. Find the mole-fraction of benzene in the vapor above the solution. **(IIT-JEE 1996)**

Solution

In the vapor phase,
1 mol (or 78 g) benzene has volume at

$$20°\text{C} = \frac{78 \times 1}{0.877} \times 2750 \text{ mL}$$

1 mol (or 92 g) toluene has volume at

$$20°\text{C} = \frac{92 \times 1}{0.867} \times 2720 \text{ mL}$$

The vapor pressures of pure benzene and toluene are

$$\frac{p_B^o}{760} \times \frac{78 \times 2750}{0.877 \times 1000} = 1 \times 0.0821 \times 293 = 74.74 \text{ mm Hg}$$

$$\frac{p_T^o}{760} \times \frac{92 \times 7720}{0.877 \times 1000} = 1 \times 0.0821 \times 293 = 22.37 \text{ mm Hg}$$

Given that $p_{\text{mix}} = 46$ mm Hg. So,

$$p_{\text{mix}} = p_B^o x_B + p_T^o x_T \Rightarrow 46 = p_B^o x_B + p_T^o (1 - x_B)$$

or

$$46 = 74.74 x_B + 22.37 (1 - x_B)$$

Solving, we get $x_B = 0.73$, therefore, $x_T = 1 - 0.73 = 0.27$.

Mole fraction of benzene in vapor phase is

$$y_B = \frac{p_B}{p_{\text{mix}}} = \frac{p_B^o x_B}{p_{\text{mix}}} = \frac{74.74 \times 0.73}{46} = 1.19$$

Solved Example 8-39

Assuming ideal behavior, calculate the vapor pressure of 1.0 molal solution of a non-volatile molecular solute in water at 50°C. The vapor pressure of water at 50°C is 0.122 atm.

Solution

$$p_{\text{solution}} = p_A = p_A^{\circ} x_A \qquad \text{(Raoult's law)}$$

By using the relation between molality and mole fraction, we have:

$$m = \frac{x_B}{x_A} \times \frac{1000}{M_A} = \frac{1 - x_A}{x_A} \times \frac{1000}{M_A}$$

$$x_A = \frac{1000}{mM_A + 1000}$$

$$= \frac{1000}{1 \times 18 + 1000} = \frac{1000}{1018} = 0.982$$

$$p_{\text{solution}} = p_A^{\circ} x_A = 0.122 \times 0.982 = 0.120 \text{ atm}$$

Solved Example 8-40

The vapor pressures of two pure liquids A and B that form an ideal solution are 300 torr and 800 torr, respectively, at temperature *T*. A mixture of the vapors of A and B for which the mole-fraction of A is 0.25 is slowly compressed at temperature T. Calculate

(a) the composition of the first drop of the condensate.

(b) the total pressure when this drop is formed.

(c) the composition of the solution whose normal boiling points is *T*.

(d) the pressure when only the last bubble of vapor remains.

(e) composition of the last bubble.

Solution

Given that $p_A^{\circ} = 300 \text{ torr}$ and $p_B^{\circ} = 800 \text{ torr}$. Now, let the mole fractions in vapor phase be y_A and y_B, then

$$y_A = 0.25 \quad \text{and} \quad y_B = 1 - 0.25 = 0.75$$

(a) By the condensation of only one drop, we can assume that vapor composition remains the same.

$$y = \frac{p_A^{\circ} x_A}{p} \quad \text{and} \quad y_B = \frac{p_B^{\circ} x_B}{p}$$

where x_A and x_B are mole fractions in solution phase. Also, $y_B = 1 - y_A$, or

$$\frac{y_A}{y_B} = \frac{p_A^{\circ} x_A}{p_B^{\circ}(1 - x_A)}$$

Putting various known values we get $x_A = 0.47$ and $x_B = 0.53$.

(b) The total pressure is $p_T = p_A^{\circ} x_A + p_B^{\circ} x_B = 300 \times 0.47 + 800 \times 0.53 = 565$ torr

(c) Atmospheric pressure is expressed as $760 = 300x_A + 800x_B$. At boiling point, vapor pressure = atmospheric pressure. So,

$$760 = 300x_A + 800(1 - x_A) \Rightarrow x_A = 0.08$$

Therefore, $x_B = 0.92$.

(d) When only the last bubble of vapor remains, we can assume composition of vapor is now the composition of the condensate.

$$y'_A = \frac{p_A^{\circ}}{p_{\text{total}}} = \frac{0.25 \times 300}{675} = 0.11$$

(e) Composition of the last bubble is $y'_B = 1 - 0.11 = 0.89$.

Solved Example 8-41

At 20°C, the vapor pressure of cyclohexane, a hydrocarbon solvent, is 66.9 mm Hg and that of toluene (another solvent) is 21.1 mm Hg. What is the vapor pressure of a solution of the two at 20°C when the mole fraction of toluene is 0.250?

Solution

$p_{\text{cyclohexane}} = x_{\text{cyclohexane}} \times p^{\circ}_{\text{cyclohexane}} = 0.750 \times 66.9 \text{ torr} = 50.2 \text{ mm Hg}$

$p_{\text{toluene}} = x_{\text{toluene}} \times p^{\circ}_{\text{toluene}} = 0.250 \times 21.1 \text{ torr} = 5.28 \text{ mm Hg}$

$p_{\text{total}} = p_{\text{cyclohexane}} + p_{\text{toluene}} = 33.5 \text{ torr} + 10.6 \text{ torr} = 55.4 \text{ mm Hg}$

Solved Example 8-42

Using the information from Solved Example 8-41, calculate the expected vapor pressure of a mixture of cyclohexane and toluene that consists of 100.0 g of each solvent.

Solution

First we need to find the moles of the cyclohexane and the moles of toluene.

$$\text{mol cylcohexane:} = (100\text{ g cyclohexane}) \times \left(\frac{1\text{ mol cyclohexane}}{84.15\text{ g cyclohexane}}\right) = 1.188\text{ mol cyclohexane}$$

$$\text{mol toluene} = (100\text{ g toluene})\left(\frac{1\text{ mol toluene}}{92.14\text{ g toluene}}\right) = 1.085\text{ mol toluene}$$

Now, find the $x_{\text{cyclohexane}}$ and the x_{toluene}

$$x_{\text{cyclohexane}} = \frac{1.188\text{ mol cyclohexane}}{1.188\text{ mol cyclohexane} + 1.085\text{ mol toluene}} = 0.523$$

$$x_{\text{toluene}} = 1 - x_{\text{cyclohexane}} = 1 - 0.523 = 0.477$$

The vapor pressures are calculated as follows:

$$p_{\text{cyclohexane}} = x_{\text{cyclohexane}} \times p^{\text{o}}_{\text{cyclohexane}} = 0.523 \times 66.9 = 35.0\text{ torr}$$

$$p_{\text{toluene}} = x_{\text{toluene}} \times p^{\text{o}}_{\text{toluene}} = 0.477 \times 21.1 = 10.1\text{ torr}$$

$$p_{\text{total}} = p_{\text{cyclohexane}} + p_{\text{toluene}} = 35.0 + 10.1 = 45.1\text{ torr}$$

Solved Example 8-43

One mole of component A and two moles of component B are mixed at 27°C to form an ideal binary solution. Calculate ΔV_{mix}, ΔH_{mix}, ΔG_{mix} and ΔS_{mix}.

Solution

Given that $n_{\text{A}} = 1$, $n_{\text{B}} = 2$, $T = 300$ K.
Since it is an ideal solution, $\Delta V_{\text{mix}} = 0$ and $\Delta H_{\text{mix}} = 0$. Also, mole fraction is given by

$$x_{\text{A}} = \frac{1}{1+2} = \frac{1}{3};\; x_{\text{B}} = \frac{2}{1+2} = \frac{2}{3}$$

We know that

$$\begin{aligned}\Delta G_{\text{mix}} &= n_{\text{total}} RT \sum x_i \log x_i \\ &= 2.303 \times 3 \times 8.314 \times 300\left[\frac{1}{2}\log\frac{1}{3} + \frac{2}{3}\log\frac{2}{3}\right] \\ &= -4765.9\text{ J}\end{aligned}$$

We know that $\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}}$

$$\text{Therefore, } -\frac{\Delta G_{\text{mix}}}{T} = \Delta S_{\text{mix}} = \frac{-4765.9}{300} = 15.88\text{ JK}^{-1}$$

Solved Example 8-44

Liquids X and Y form an ideal solution. The vapor pressure of X and Y at 100°C are 300 and 100 mm of Hg, respectively. A solution composed of 1 mol of X and 1 mol of Y at 100°C is collected and condensed. The condensate is heated at 100°C and vapor is again condensed to form a liquid A. What is mole fraction of X in A?

Solution

Initially in the liquid phase, the pressure and mole fractions are given by

$$p^{\circ}_{\text{X}} = 300\text{ mm} \quad \text{and} \quad p^{\circ}_{\text{Y}} = 100\text{ mm}$$

$$x_{(\text{X,l})} = \frac{1}{2} \quad \text{and} \quad x_{(\text{Y,l})} = \frac{1}{2}$$

Therefore,

$$p_{\text{X}} = 300 \times \frac{1}{2} = 150 \quad \text{and} \quad p_{\text{Y}} = 100 \times \frac{1}{2} = 50$$

Thus, $p_{\text{total}} = 150 + 50 = 200$ mm

We now calculate mole fraction of X and Y in vapor phase, using Dalton's law, as

$$\begin{aligned}p_{\text{X}} &= x_{(\text{X,vap})} \times p_{\text{total}} \\ 150 &= x_{(\text{X,vap})}(200)\end{aligned}$$

$$x_{(\text{X,vap})} = \frac{3}{4}$$

Similarly, $x_{(\text{Y,vap})} = \dfrac{1}{4}$

When this is condensed, the mole fraction in this vapor phase will be equal to the mole fraction of the new liquid phase. Let the mole fractions in new liquid phase be $x_{1(\text{X,l})}$ and $x_{1(\text{Y,l})}$. Then

$$x_{1(\text{X, l})} = x_{(\text{X,vap})} = \frac{3}{4}$$

$$x_{1(\text{Y, l})} = x_{(\text{Y,vap})} = \frac{1}{4}$$

Therefore,

$$p_{\substack{X\\(\text{new})}} = \frac{3}{4} \times p^{\circ}_{X} = \frac{3}{4} \times 300 = 225$$

$$p_{\substack{Y\\(\text{new})}} = \frac{1}{4} \times p^{\circ}_{Y} = \frac{1}{4} \times 100 = 25$$

Thus, $p_{\text{total}} = 250$ mm.

Now when the condensate is heated to vapor, let the mole fraction of X and Y in the new vapor phase be $x_{1(\text{X, vap})}$ and $x_{1(\text{Y, vap})}$. Then, according to Dalton's law

$$x_{1(\text{X,vap})} = \frac{p_{\text{X(new)}}}{p_{\text{total}}} = \frac{225}{250} = 0.9$$

So if it is again condensed, then

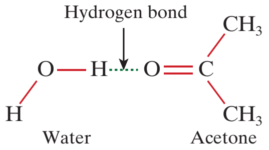
$x_{1(\text{X, vap})} = x_{2(\text{X, l})}$ = mole fraction of X in liquid A = 0.9

8.10 | NON-IDEAL SOLUTIONS

Solutions are non-ideal if they do not obey Raoult's law over the entire composition range. In preparation of such solutions, heat is either given out or absorbed ($\Delta H_{\text{mix}} \neq 0$) and the volume of the final solution is not equal to the sum of volume of individual components of the solution ($\Delta V_{\text{mix}} \neq 0$). The vapor pressure of the solution is either higher or lower than that predicted by Raoult's law. Depending on type of deviation of from ideal behavior, non-ideal solutions may be classified as showing **negative deviation** (lower vapor pressure than predicted) or **positive deviation** (higher vapor pressure than predicted).

1. **Negative deviation:** In such solutions of component A and B, the A–B interactions are stronger than the A–A and B–B interactions. Since the interactions between solute and solvent are stronger than solute–solute and solvent–solvent interactions, lesser number of the molecules escape in pure state. As a result, the vapor pressure of the solution is lower than that predicted by Raoult's law. For example, acetone and water are liquids that form a solution exothermically (ΔH_{soln} is negative). With these liquids, the step involving interactions of acetone with water releases more energy than the sum of the interactions between component molecules, that is, water–water and acetone–acetone. This is because molecules of water and acetone attract each other more strongly than acetone molecules attract each other. This is further due to the formation of hydrogen bonds by water molecules with acetone molecules in the solution, but acetone molecules cannot form hydrogen bonds with other acetone molecules in the pure liquid.

   Another example of negative deviation is that of solution of phenol with aniline. Here, the hydrogen bonding between acidic proton on phenol with the lone pair on nitrogen (intermolecular hydrogen bonding) is stronger than the hydrogen bonding between aniline–aniline or phenol–phenol molecules (intramolecular hydrogen bonding). Some other examples are: chloroform + benzene and acetic acid + pyridine. The variation in vapor pressures of the components A and B of the solution with the mole fraction for negative deviation is shown in Fig. 8.14.



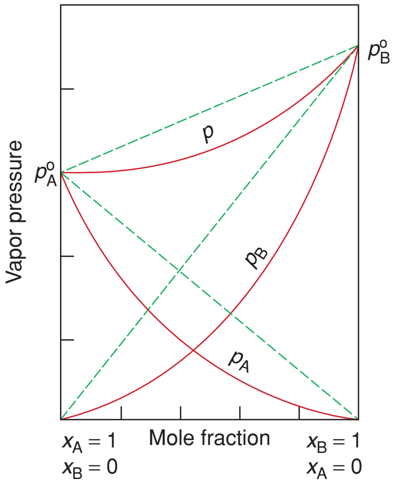


Figure 8.14 Change of vapor pressure with mole fraction in a non-ideal solution showing negative deviations.

2. **Positive deviation:** In such solutions of component A and B, the A–B interactions are weaker than the A–A and B–B interactions. Since the interactions between solute and solvent are weaker than interactions between solute and solute or solvent and solvent, some of the molecules escape in pure state. As a result, the vapor pressure of the solution is higher than that predicted by Raoult's law. Mixture of ethanol and hexane is an example of this kind. Ethanol molecules attract each other more strongly than they can attract hexane molecules. Hexane molecules cannot push their way into ethanol without breaking up some of the hydrogen bonding between ethanol molecules. Hence, ethanol and hexane form a solution endothermically. In this case, the release of energy in association of ethanol with hexane is not enough to compensate for the

energy demands required to overcome the attractive interactions between the components, and the solution cools as it forms. Other examples of mixtures showing positive deviation are: acetone + carbon disulphide; carbon tetrachloride + benzene; carbon tetrachloride + toluene; etc. The variation in vapor pressures of the components A and B of the solution with the mole fraction for positive deviation is shown in Fig. 8.15.

From the figure, we can see that vapor pressure of the solution is lower than that predicted by Raoult's law (dashed lines show ideal behavior).

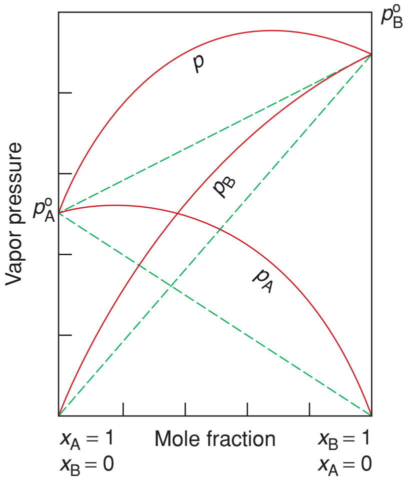


Figure 8.15 Change of vapor pressure with mole fraction in a non-ideal solution showing positive deviation from ideality.

Azeotropic (Constant Boiling) Mixtures

Some liquid solutions of two (or more) components have a composition that does not change on distillation. This is because they have the same composition in solution as well as in vapor phase. Such mixtures are **azeotropic** or **constant boiling mixtures** and are known as **azeotropes**. It is difficult to separate the components of these mixtures by fractional distillation as both the components vaporize at the same temperature that is the boiling point of the mixture. The azeotropes have a characteristic boiling point which is either higher (positive deviation) or lower (negative deviation) than any of its constituents and are called minimum boiling and maximum boiling azeotropes, respectively. For example, ethanol, normally obtained on distillation, is an azeotrope of composition ethanol (95%) + water (5%). It is a maximum boiling (negative deviation) azeotrope because it boils at 78.2°C; whereas the boiling point of pure ethanol is 78.4°C and that of water is 100°C (Fig. 8.16). Similarly, mixture of nitric acid and water exist as an azeotrope of composition nitric acid (68%) + water (32%) by mass. It is a minimum boiling (positive deviation) azeotrope because it boils at 120.5°C, whereas the boiling point of pure nitric acid is 86°C and that of water is 100°C.

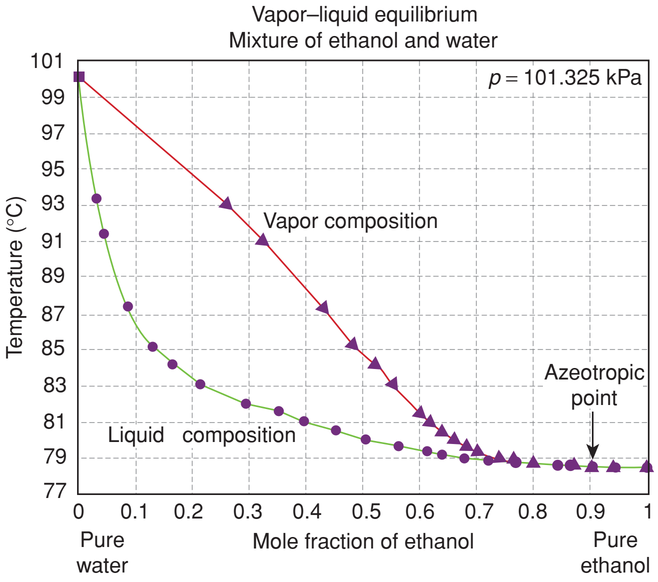


Figure 8.16 Azeotropic mixture of water and ethanol.

Note: Non-ideal solutions often form azeotropes. Azeotropic mixtures cannot be easily separated by ordinary distillation methods. For example, in distillation of ethanol and water mixture, ethanol is recovered up to about 89%, beyond which the mixture becomes azeotropic. A separation technique called azeotropic distillation is used for separation of these mixtures.

Types of Azeotropes

These are mainly two types of azeotropes, minimum boiling and maximum boiling and these are discussed as follows.

1. **Minimum boiling azeotropes:** These are characteristics of non-ideal solution showing positive deviation from ideal solution, that is, $\Delta H_{mix} > 0$ and $\Delta V_{mix} > 0$. These solutions will boil at a lower boiling point than any of its pure components. The vapor pressure will be greater than any of its pure components. For example, in a non-ideal binary solution of ethanol and H_2O, the pressure vs. mole fraction (of water) curve is as shown in Fig. 8.17(a). Here, the liquid phase is denoted by upper curve and vapor phase by lower curve.

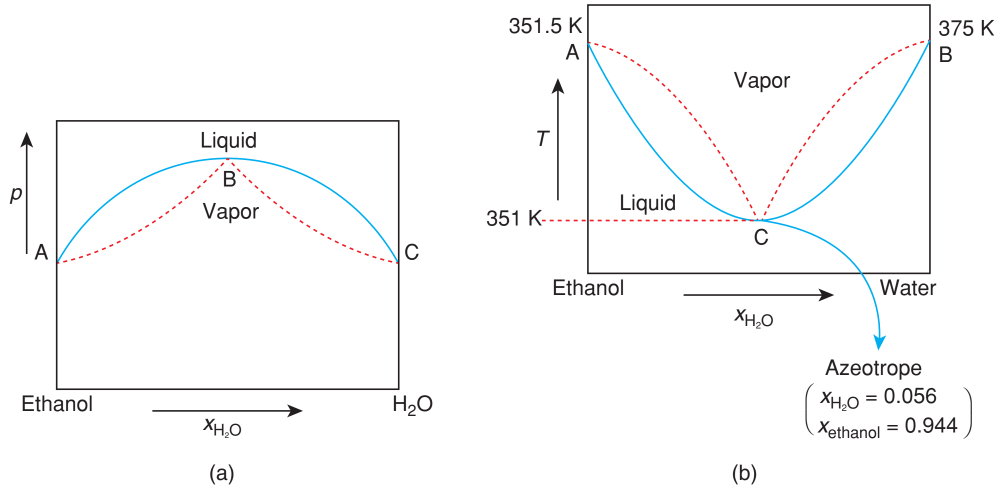


Figure 8.17 Ethanol-water non-ideal binary solution (minimum boiling azeotrope). (a) Pressure vs. mole fraction (water) curve. (b) Temperature vs. mole fraction (water) curve.

In the temperature vs. mole fraction curve shown in Fig. 8.17(b) also, vapor phase is denoted by upper curve and liquid phase by lower curve.

We can also understand that it will not be possible to separate this solution into pure components A and B completely, even though, they have different boiling points. The fractional distillation will give one of the pure components (A or B) and azeotropic mixture C.

In the above example we can get ≅ 95% ethanol by volume of ethanol. At this composition, the liquid and vapor have the same composition and thus it not possible to further separate water from ethanol.

2. **Maximum boiling azeotropes:** These are shown by non-ideal solutions showing negative deviation from ideal solution, that is, $\Delta H_{mix} < 0$ and $\Delta V_{mix} < 0$. These solutions will boil at a higher boiling point than any of its pure components. The vapor pressure will be lower than any of the pure components.

For example, consider a non-ideal binary solution of HNO_3 and H_2O. The pressure vs. mole fraction (HNO_3) and temperature vs. mole fraction (HNO_3) curves are shown in Fig. 8.18 (a) and (b), respectively.

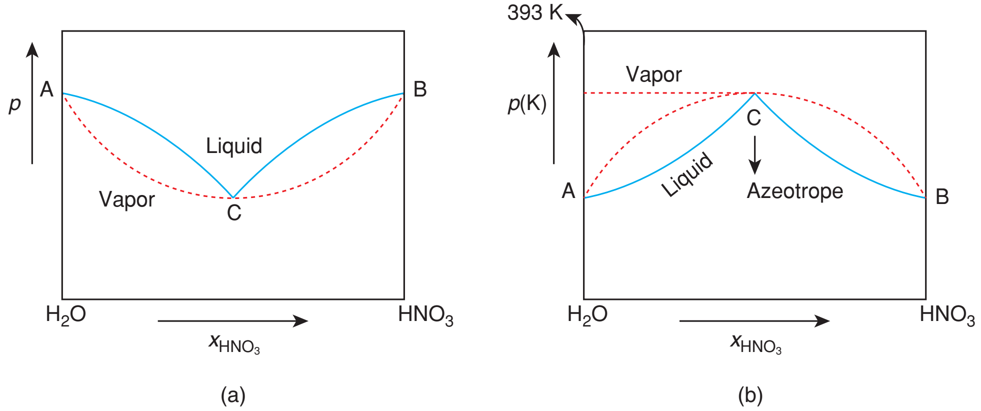


Figure 8.18 Nitric acid-water non-ideal binary solution (maximum boiling azeotrope). (a) Pressure vs. mole fraction (water) curve. (b) Temperature vs. mole fraction (water) curve.

In this case also, it will not be possible to obtain pure A and pure B by fractional distillation. In the above case, the composition of azeotrope is 68% HNO_3 and 32% of H_2O by mass. We cannot separate HNO_3 from H_2O any further.

8.11 | COLLIGATIVE PROPERTIES AND DETERMINATION OF MOLAR MASS

The solution formed by the addition of a non-volatile solute to a solvent has a lower freezing point, a higher boiling point and a lower vapor pressure than that of the pure solvent. These effects are related and are known as colligative properties. The **colligative properties** are properties that depend only on the number of solute particles in a solution, but are independent of the nature of those particles. The term colligative is derived from the latin word *colligare*, which means to bind together. In this section, we will discuss the four colligative properties of solutions: vapor pressure lowering, boiling point elevation, freezing point depression and osmotic pressure.

Note: The basic assumption for describing colligative properties of dilute solutions is that the solute is non-volatile and is not present in the vapor phase at all.

Relative Lowering of Vapor Pressure

The presence of a non-volatile solute in a solvent lowers the equilibrium vapor pressure from that of the pure solvent. It is not hard to understand why this occurs based on what we have discussed about the interactions between the solute and solvent. Because of various attractive forces, solvent molecules surround solute molecules or ions. Solute molecules or ions thus tend to tie up the solvent molecules, which in effect prevents them from escaping to vapor. The more solute particles present, the more solvent molecules that are held in the liquid phase. Thus the solution has a lower equilibrium vapor pressure than the pure solvent (Fig. 8.19). As we might predict from this model, the more solute particles present, the lower the vapor pressure of the solution.

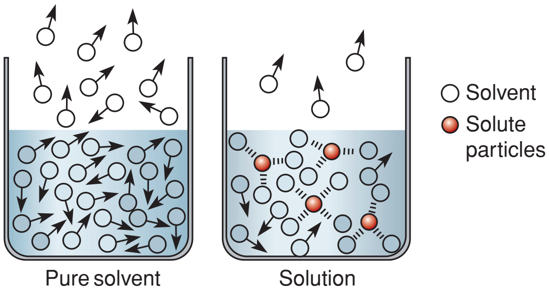


Figure 8.19 Vapor pressure lowering.

We can establish the relation between relative lowering of vapor pressure with the mole fraction of the solute based on Raoult's law and show that the relative lowering depends only on concentration of the solute and not on nature of solute. According to Raoult's law

$$p_A = x_A p_A^\circ$$

The lowering of vapor pressure of the solvent Δp_A is given by

$$\Delta p_A = p_A^\circ - p_A$$

Substituting for p_A, we get

$$\Delta p_A = p_A^\circ - x_A p_A^\circ = p_A^\circ (1 - x_A) \tag{8.31}$$

We know that the sum of mole fractions of the solute and solvent is unity, that is, $x_A + x_B = 1$ or $x_B = 1 - x_A$. Using the relation in Eq. (8.31), the lowering of vapor pressure of the solvent can be expressed as

$$\Delta p_A = p_A^\circ x_B$$

or

$$\frac{\Delta p_A}{p_A^\circ} = \frac{p_A^\circ - p_A}{p_A^\circ} = x_B \tag{8.32}$$

Thus, we can see that the relative lowering of vapor pressure (LHS of the equation) depends only on the mole fraction of the solute (RHS of the equation). This relation can also be expressed in terms of molar masses of the solute and is used to determine the molar mass of an unknown solute present in a solution by measuring the lowering of vapor pressure. If n_A and n_B are the number of moles of solvent and solute respectively, then

$$x_B = \frac{n_B}{n_A + n_B}$$

Substituting in Eq. (8.32), we get

$$\frac{p_A^\circ - p_A}{p_A^\circ} = \frac{n_B}{n_A + n_B} \tag{8.33}$$

For dilute solutions, as the number of moles of solute is very less as compared to number of moles of solvent, the equation reduces to

$$\frac{p_A^\circ - p_A}{p_A^\circ} = \frac{n_B}{n_A} = \frac{w_B \times M_A}{M_B \times w_A} \tag{8.34}$$

where w_A and w_B are the masses of solvent and solute taken and M_A and M_B are the molar masses of the solvent and solute.

Mathematical formula for relative lowering when solution is not dilute:

$$\frac{p_A^\circ - p_A}{p_A^\circ} = \frac{n_B}{n_A + n_B}$$

or
$$\frac{p_A^\circ}{p_A^\circ - p_A} = \frac{n_A + n_B}{n_B} = 1 + \frac{n_A}{n_B}$$

or
$$\frac{p_A^\circ - p_A}{p_A} = \frac{n_B}{n_A}$$

Ostwald and Walker Method

In Ostwald and Walker method, we use two sets of bulbs. The first set of bulbs consists of solution and second set of bulbs consists of the pure solvent. Each set is weighed accurately and both sets are connected to each other. They are then connected to a weighed set of guard tubes containing dehydrating agents like P_2O_5, $CaCl_2$, etc. (Fig. 8.20).

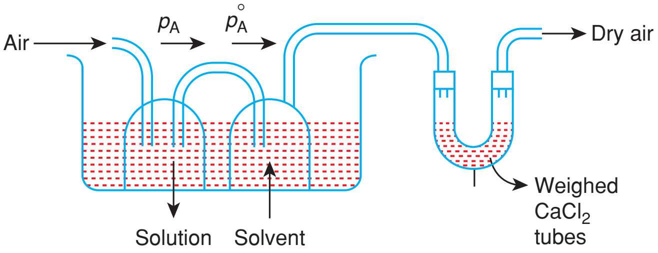


Figure 8.20 Ostwald–Walker method.

A current of pure dry air is passed through the series of bulbs and the air gets saturated with vapors from each set. The air takes up an amount of vapors proportional to the vapor pressure of solution. When it is passed through pure solvent, it takes up amount of vapors proportional to difference in vapor pressure of pure solvent and that of solution. Therefore,

Loss in mass of solution $\propto p_A$

Loss in mass of solvent $\propto p_A^\circ$

Total loss in both solution solvent $\propto p_A^\circ + p_A$

Therefore,
$$\frac{p_A^\circ - p_A}{p_A^\circ} = \frac{\text{Loss in mass of solvent}}{\text{Total loss in mass in solution + solvent}}$$

Also gain in mass of $CaCl_2$ tube $\propto p^\circ_A$. Therefore,

$$\frac{p^\circ_A - p_A}{p^\circ_A} = \frac{\text{Loss in mass of solvent}}{\text{Gain in mass of CaCl}_2\text{ tube}}$$

Effect of Lowering of Vapor Pressure on Freezing and Boiling Points

The lowering of the vapor pressure produced by the presence of a non-volatile solute affects both the boiling and freezing points of a solution. This is illustrated for water in Fig. 8.21.

The solid blue lines in the figure correspond to the three equilibrium lines in the phase diagram for pure water. Adding a non-volatile solute lowers the vapor pressure of the solution, giving a new liquid–vapor equilibrium line for the solution, which is shown as the red line connecting points *A* and *B*.

If we look at where the solid–liquid and liquid–vapor lines cross the 1 atm (760 torr) pressure line, we can find the normal freezing and boiling points. For water (the blue lines), the freezing point is 0°C and the boiling point is 100°C. Notice that the solid–liquid line for the solution meets the 760 torr line at a temperature *below* 0°C. In other words, the freezing point of the solution is below that of pure water. The amount by which the freezing point is lowered is called the **freezing point depression**, and is given the symbol ΔT_f. Similarly, we can see that the liquid–vapor line for the solution crosses the 760 torr line at a temperature *above* 100°C, so the solution boils at a higher temperature than pure water. The amount by which the boiling point is raised is called the **boiling point elevation**. It is given the symbol ΔT_b.

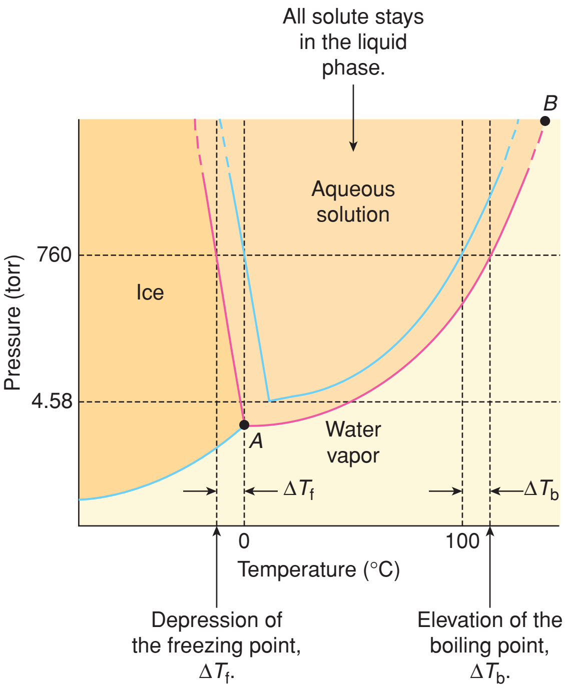


Figure 8.21 Phase diagram for water and an aqueous solution.

Solved Example 8-45

The vapor pressure of pure benzene at a certain temperature is 640 mm Hg. A non-volatile non-electrolyte solid weighing 2.175 g is added to 39.0 g of benzene. The vapor pressure of the solution is 600 mm Hg. What is the molecular weight of the solid substance? **(IIT-JEE 1990)**

Solution

According to Raoult's law

$$\frac{p^\circ_A - p}{p^\circ_A} = x_B = \frac{n_B}{n_A + n_B}$$

Here, $p^\circ_A = 640$ mm Hg and $p = 600$ mm Hg. Also, given that $w_B = 2.175$ g, $w_A = 39$ g, $M_A = 78$ g mol^{-1}. Therefore,

$$\frac{640-600}{640} = \frac{\dfrac{2.175}{M_B}}{\dfrac{2.175}{M_B} + \dfrac{39}{78}} \Rightarrow M_B = 65.25 \text{ g mol}^{-1}$$

Solved Example 8-46

What weight of the non-volatile solute, urea (NH_2–CO–NH_2) needs to be dissolved in 100 g of water, in order to decrease the vapor pressure of water by 25%? What will be the molality of the solution. **(IIT-JEE 1993)**

Solution

The lowering of vapor pressure on addition of solute is given by

$$\frac{p^\circ - p}{p^\circ} = x_B = \frac{w_B/M_B}{w_A/M_A + w_B/M_B}$$

Here w_B and M_B are weight and molecular weight of solute, w_A and M_A are weight and molecular weight of solvent. Also, p is the pressure of solution and p° is the normal (initial) vapor pressure.

Therefore, pressure of solution $= \dfrac{75}{100} \times p^\circ = \dfrac{3}{4} p^\circ$ (as vapor pressure decrease by 25%).

Also given that M_B = 60 g mol^{-1}, M_A = 18 g mol^{-1}, w_A = 100 g and w_B = 111 g. Hence, molality is

$$\text{Molality} = \frac{\text{Number of moles of solute}}{\text{Weight of solvent}} \times 100$$

$$= 18.52 \text{ molal}^{-1}$$

Elevation of Boiling Point

The boiling point of a liquid is the temperature at which the liquid and vapor phases are in equilibrium with each other at a given pressure. At the boiling point, the vapor pressure of the liquid is equal to the applied pressure on the liquid. The boiling point at standard pressure (1 atm) is called the normal boiling point.

Adding salt to water raises the boiling point of the solution. Raising the boiling point means that food cooks a little faster, depending how much salt is dissolved. *A direct effect of the lowered vapor pressure of a solution is a higher boiling point than that of the solvent*. Recall that the normal boiling point of water is 100°C, which is the temperature at which its vapor pressure is equal to 760 mm Hg. An aqueous solution, on the other hand, would not have a vapor pressure of 760 mm Hg at 100°C – it would be lower than 760 mm Hg. Thus, the solution would have to be heated above 100°C for the vapor pressure to reach 760 mm Hg and begin to boil. Again, the more concentrated the solution, the lower the vapor pressure and the higher the boiling point (Fig. 8.18). The difference in the boiling point of a solution containing a non-volatile solute and the boiling point of the pure solvent is known as ***boiling-point elevation*** (ΔT_b). It is given by the equation

$$\Delta T_b = T_b - T_b^\circ$$

where ΔT_b is the number of celsius (or kelvin) degrees that the boiling point is raised, T_b is the boiling point of the solution and T_b° is the boiling point of pure solvent. Since boiling point elevation is a colligative property, its magnitude is proportional to the relative amount of solvent and solute.

Relation with molality: Experiments have shown that boiling point elevation is directly proportional to the molal concentration of the solute in a solution and is given by

$$\Delta T_b = K_b m \qquad (8.35)$$

where K_b is a constant characteristic of the solvent (for water K_b = 0.512 molal is molality). Molality (m) is the preferred concentration expression (rather than mole fraction or percent by mass) because of the resulting simplicity of the equations relating ΔT to concentration. This equation works reasonably well only for dilute solutions. The constant K_b is called boiling point elevation constant or *Ebullioscopic* constant. For example, K_b for water is 0.512 K kg mol^{-1}, a 1 molal aqueous solution at 1 atm pressure boils at (373 + 0.51) K or 373.51 K, and a 2 molal solution should boil at 374.02 K. Values of K_b for some common solvents are given in Table 8.4.

Table 8.4 Values of K_b for some common solvents

Solvent	Boiling point of pure solvent (K)	Boiling point elevation constant K_b (K kg mol^{-1})
Chloroform	334.4	3.63
Benzene	353.3	2.53
Carbon tetrachloride	350.0	5.03
Acetone	329.1	0.86
Cyclohexane	353.7	2.79
Ethanol	351.5	1.20
Diethyl ether	307.8	2.93
Water	373	0.512

Determination of molar mass: The elevation in boiling point can be used to measure the molecular mass of an unknown solute present in the solution. If w_B g is the amount of solute of molar mass M_B dissolved in mass w_A g of the solvent of molar mass M_A, then the molality of the solution is

$$m = \frac{w_B / M_B}{w_A / 1000} = \frac{1000 \times w_B}{M_B \times w_A}$$

Substituting this value of m in Eq. (8.35), we get

$$\Delta T_b = \frac{K_b \times 1000 \times w_B}{M_B \times w_A}$$

or

$$M_B = \frac{1000 \times w_B \times K_b}{\Delta T_b \times w_A} \tag{8.36}$$

Thus molecular mass of the solute can be determined if we measure the boiling point elevation of a solution containing known masses of solute and solvent.

Note: Relation between K_b and enthalpy of vaporization. For dilute solutions, $m \to 0$, so $T_b \to T_b^{\circ}$. The limiting value of $(\partial T_b/\partial m)_{m\to 0}$ is K_b and depends upon the characteristics of the solvent.

$$K_b = \left(\frac{\partial T_b}{\partial m}\right)_{m\to 0} = \frac{R T_b^{\circ 2} M_A}{1000 \times \Delta H_{\text{vap}}}$$

Mathematical Derivation of Boiling Point Elevation

Figure 8.22 shows the plot for variation of vapor pressure with temperature of pure solvent, solution 1 and solution 2. At temperature T_0, the vapor pressures of pure solvent, solution 1 and solution 2 are respectively, p_0, p_1 and p_2.

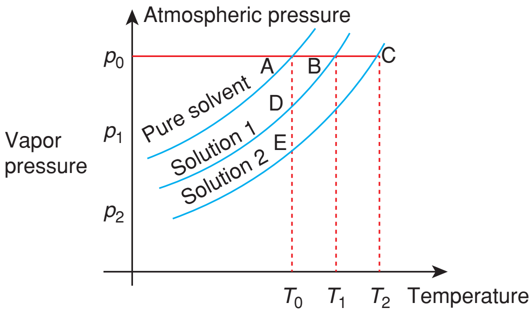


Figure 8.22 Vapor pressure vs. temperature curve for pure solvent, solution 1 and solution 2.

From similarly of triangles

$$\frac{AC}{AB} = \frac{AE}{AD}$$

$$\frac{T_2 - T_0}{T_1 - T_0} = \frac{p^{\circ} - p_2}{p^{\circ} - p_1}$$

$$\frac{\Delta T_2}{\Delta T_1} = \frac{\Delta p_2}{\Delta p_1}$$

From Raoult's law

$$\frac{p_A^{\circ} - p_A}{p_A^{\circ}} = \frac{w_B M_A}{M_B w_A}$$

where, p_A° = vapor pressure of pure solvent
p_A = vapor pressure of solution
w_B = weight of solute, M_B = mol. wt. of solute
w_A = weight of solvent, M_A = mol. wt. of solvent

Therefore,

$$p_A^\circ - p_A = \left(\frac{w_B M_A}{M_B \cdot w_A}\right) p_A^\circ$$

Here, p_A° and M_A are constant, so

$$\Delta p = p_A^\circ - p_A \propto \frac{w_B}{M_B w_A}$$

$$\Delta T \propto \Delta p$$

Therefore,

$$\Delta T \propto \frac{w_B}{M_B w_A}$$

$$\Delta T = K \frac{w_B}{M_B \cdot w_A}$$

where K is the elevation constant.

If we take, $\frac{w_B}{M_B} = 1$, that is, one mole of solute and w_A = 1000 gram or 1 kg, then

$$\Delta T = \frac{K}{1000} = K_b$$

where K_b is the molal elevation constant. Therefore,

$$\Delta T = \frac{1000\ K_b \cdot w_B}{M_B \cdot w_A}$$

$$\Delta T = \text{molality} \times K_b$$

Solved Example 8-47

At what temperature will a 10% aqueous solution of sugar ($C_{12}H_{22}O_{11}$) boil? [$K_b(H_2O) = 0.52°C\ \text{molal}^{-1}$]

Solution

A 10% solution contains 10 g sugar and 90 g water.

$$10\ \text{g}\ C_{12}H_{22}O_{11} \div 342\ \text{g mol}^{-1} = 0.029\ \text{mol}\ C_{12}H_{22}O_{11}$$

$$90\ \text{g}\ H_2O \times 1\ \text{kg}/1000\ \text{g} = 0.090\ \text{kg}\ H_2O$$

Hence, molality is $m = \frac{0.029\ \text{mol}}{0.090\ \text{kg}} = 0.32\ \text{mol kg}^{-1}$

Now, elevation in boiling point is
$\Delta T_b = K_b \times m = 0.52°C\ \text{molal}^{-1} \times 0.32\ \text{molal} = 0.16°C$
Therefore the boiling point = 100 + 0.16 = 100.16°C

Solved Example 8-48

Nitrobenzene is formed as the major product along with a minor product in the reaction of benzene with a hot mixture of nitric acid and sulphuric acid. The minor product consists of carbon; 42.86%, hydrogen: 2.40%, nitrogen: 16.67%, and oxygen: 38.07% (i) Calculate the empirical formula of the minor product, (ii) When 5.5 g of the minor product is dissolved in 45 g of benzene, the boiling point of the solution is 1.84°C higher than that of pure benzene. Calculate the molar mass of the minor product and determine its molecular and structural formula. (Molal boiling point elevation constant of benzene is 2.53 K kg mol^{-1}) **(IIT-JEE 1999)**

Solution

Element	%	Relative no. of atoms	Simple ratio
C	42.86	$\frac{42.86}{12} = 3.57$	$\frac{3.57}{1.19} = 3$

Element	%	Relative no. of atoms	Simple ratio
H	2.40	$\frac{2.40}{1} = 2.40$	$\frac{2.40}{1.19} = 2$
N	16.67	$\frac{16.67}{14} = 1.19$	$\frac{1.19}{1.19} = 1$
O	38.67	$\frac{38.07}{16} = 2.38$	$\frac{2.38}{1.19} = 2$

Therefore, empirical formula of the minor product is $C_3H_2NO_2$.

Molar empirical formula mass of the minor product = 84 g mol^2 $(12 \times 3 + 2 \times 1 + 14 + 16 \times 2)$

Let M be the molar mass of the minor product. For 5.5 g of the minor product dissolved in 45 g benzene.

The molality m of the solution $\frac{5.5\ \text{g}/M_B}{0.045\ \text{kg}}$ and elevation in boiling point is $\Delta T_b = K_b m = 1.84$ K.

Therefore,

$$1.84 = 2.53 \times \frac{5.5\ \text{g}/M_B}{0.045\ \text{kg}} \Rightarrow M_B = 168\ \text{g mol}^{-1}$$

Now, empirical formula mass $\times\, n$ = molecular mass

Number of unit of empirical (n) formula in molecular formula $= \frac{168\,\text{g mol}^{-1}}{84\,\text{g mol}^{-1}} = 2$

Hence, the molecular formula of the minor product is $2 \times C_3H_2NO_2 = C_6H_4(NO_2)_2$. So, the product is *m*-dinitrobenzene.

Solved Example 8-49

How many grams of glucose (molar mass 180.2 g mol^{-1}) must be dissolved in 250 g of water to raise the boiling point to 102.36°C? [K_b (H_2O) = 0.52 °C molal^{-1}]

Solution

We know that $\Delta T_b = K_b \times m = 0.52°\text{C molal}^{-1} \times m = 2.36°\text{C} \Rightarrow m = 4.54$ molal

To find the number of grams of glucose, first we need to find the number of moles of glucose.

mol glucose = (m solution) × (kg solvent)

mol glucose = (4.54 molal) × (0.250 kg H_2O) = 1.135 mol glucose

g glucose = $(1.135\ \text{mol glucose})\left(\frac{180.9\ \text{g glucose}}{1\ \text{mol glucose}}\right) =$ 205.32 g glucose

Solved Example 8-50

An aqueous solution of urea is found to boil at 100.52°C. Given K_b for water is 0.52°C molal^{-1}, what is the mole fraction of urea in the solution?

Solution

Given that $\Delta T_b = 0.52°\text{C}$ and $K_b = 0.52°\text{C molal}^{-1}$. Substituting these values in the expression, we get

$$\Delta T_b = K_b \times \text{Molality} \Rightarrow 0.52 = 0.52 \times m \Rightarrow m = 1\ \text{molal}$$

The number of moles of urea or mole fraction (m × mol. wt.)/1000 = 1 × 18/1000 = 0.018 mol.

Solved Example 8-51

The molal boiling point constant for water is 0.52°C kg mol^{-1}. When 0.1 mol of sugar is dissolved in 200 g of water, the solution boils at what temperature?

Solution

According to elevation in boiling point, $\Delta T_b = K_b \times m$ where m(molality) = 0.1/200

$$\Delta T_b = 0.52 \times \frac{0.1}{200} = 0.26°\text{C}$$

Now,

$$\Delta T_b = T_b - T_b^{o} \Rightarrow 0.26 = T_b - 100 \quad (100°\text{C for water})$$

Therefore, boiling point of the solution, $T_b = 100 + 0.26 = 100.26°\text{C}$

Depression in Freezing Point

The freezing point of a liquid is the temperature at which a liquid of specific composition turns into a solid. At this temperature, the liquid and solid phases of a substance of specified composition are in equilibrium at atmospheric pressure. In countries experiencing extreme cold conditions, the icy, cold winds of winter can be very hard on automobiles. If there is not enough antifreeze in the radiator, the coolant water may freeze. This could ruin the radiator and even crack the engine block, because water expands when it freezes. Similarly, when we spread salt on ice-covered streets or sidewalks. In both of these cases, we take advantage of the fact that solutions have lower freezing points than pure solvents. *Just as the boiling point of a solution is higher than that of the pure solvent, the freezing point is lower* (see Fig. 8.21).

The difference in the freezing point of a solution containing a non-volatile solute and the freezing point of the pure solvent is known as ***freezing point depression*** (ΔT_f) is given by the equation

$$\Delta T_f = T_f^\circ - T_f$$

where ΔT_f the number of Celsius (or Kelvin) degrees that the freezing point is depressed, T_f is the freezing point of the solution and T_f° is the freezing point of pure solvent. Since freezing point depression is a **colligative property, its magnitude is proportional to the relative amount of solvent and solute**.

Relation with molality: Experiments have shown that freezing point depression is directly proportional to the molal concentration of the solute in a solution and given by

$$\Delta T_f = K_f m \tag{8.37}$$

where K_f is constant characteristic of the solvent and m is molality. This equation holds good only for dilute solutions. The constant K_f is called freezing point depression constant or *cryoscopic* constant. Thus, the value of K_f for a given solvent corresponds to the number of degrees of freezing point lowering for each molal unit of concentration. The K_f for water is 1.86 K molal^{-1}. A 1 molal solution in water freezes at 1.86 K *below* the normal freezing point of 273 K, or at 271.14 K. A 2 molal solution should freeze at 269.28 K. Values of K_f for some common solvents are given in Table 8.5.

Note: The values of both K_f and K_b are characteristic of each solvent. The units of constants K_f and K_b are K kg mol^{-1} or °C $(\text{molal})^{-1}$.

Table 8.5 Values of K_f for some common solvents

Solvent	Freezing point of pure solvent (K)	Freezing point depression constant K_f (K kg mol^{-1})
Chloroform	209.6	4.79
Benzene	278.5	5.12
Carbon tetrachloride	250.5	31.8
Water	273.0	1.86
Camphor	451.0	48.5
Ethanol	155.7	1.86
Diethyl ether	156.9	1.79
Water	273.0	1.86

Determination of molar mass: The depression in freezing point can be used to measure the molecular mass of an unknown solute present in the solution. If w_B grams is the amount of solute of molar mass M_B dissolved in mass w_A grams of the solvent of molar mass M_A, then the molality of the solution is

$$m = \frac{w_B/M_B}{w_A/1000} = \frac{1000 \times w_B}{M_B \times w_A}$$

Substituting this value of m in Eq. (8.37), we get

$$\Delta T_f = \frac{K_f \times 1000 \times w_B}{M_B \times w_A}$$

or

$$M_B = \frac{1000 \times w_B \times K_f}{\Delta T_f \times w_A} \tag{8.38}$$

Thus molecular mass of the solute can be determined if we measure the freezing point depression of a solution containing known masses of solute and solvent.

Note: Relation between K_f and enthalpy of fusion: For dilute solutions, $m \to 0$, so $T_f \to T_f^o$. The limiting value of $(\partial T_f/\partial m)_{m\to 0}$ is K_f and depends upon the characteristics of the solvent.

$$K_f = \left(\frac{\partial T_f}{\partial m}\right)_{m\to 0} = \frac{RT_f^{o2} M_A}{1000 \times \Delta H_{\text{fusion}}}$$

Mathematical Derivation of Freezing Point Depression

Figure 8.23 shows the plot for variation of vapor pressure with temperature of pure solvent, solution 1 and solution 2. At temperature T_0, the vapor pressures of pure solvent solution 1 and solution 2 are respectively, p_0, p_1 and p_2.

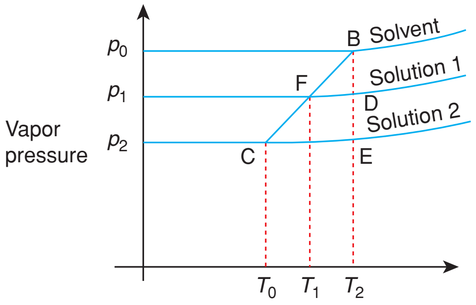


Figure 8.23

Similar to derivation of elevation of boiling point, we have from similarity of triangles

$$\frac{\text{EC}}{\text{DF}} = \frac{\text{BE}}{\text{BD}}$$

$$\frac{T_0 - T_2}{T_0 - T_1} = \frac{p^\circ - p_2}{p^\circ - p_1}$$

$$\frac{\Delta T_2}{\Delta T_1} = \frac{\Delta p_2}{\Delta p_1}$$

$$\Delta T \propto \Delta p$$

$$\frac{p_A^\circ - p_A}{p_A^\circ} = \frac{w_B M_A}{M_B w_A}$$

$$p_A^\circ - p_A = \left(\frac{w_B M_A}{M_B \cdot w_A}\right) p_A^\circ$$

$$\Delta p \propto \Delta T \propto \frac{w_B}{M_B w_A}$$

$$\Delta T = K \frac{w_B}{M_B \cdot w_A}$$

where K is the depression constant.

If we take $\frac{w_B}{M_B} = 1$ (1 mole of solute), $w_A = 1000$ grams.

Therefore, $\Delta T = \frac{K}{1000} = K_f$

Here K_f is the molal depression constant.

$$\Delta T = 1000\ K_f \frac{w_B}{M_B \cdot w_A}$$

$$\Delta T = \text{Molality} \times K_f$$

Solved Example 8-52

What inference can be made from the depression of freezing point experiment? **(IIT-JEE 1999)**

Solution

According to Raoult's law, when a non-volatile solute is added to a pure solvent to form a solution vapor pressure of solution decreased compared to that of a solution. At the freezing point, only solvent freezes in a solution, while the solute does not.

(a) The vapor pressure of the solution is less than that of pure solvent

(b) Only solvent molecules solidify at the freezing point

Solved Example 8-53

Estimate the freezing point of a solution made from 10.0 g of urea, $CO(NH_2)_2$ (molar mass 60.06 g mol^{-1}), and 125 g of water. ($K_f = 1.86°C\ \text{molal}^{-1}$)

Solution

We know that $\Delta T_f = K_f m$. The number of moles of urea dissolved in 125 g or 0.125 kg of water is

$$10.0\text{ g } CO(NH_2)_2 \times \frac{1\text{ mol } CO(NH_2)_2}{60.06\text{ g } CO(NH_2)_2}$$
$$= 0.166\text{ mol } CO(NH_2)_2$$

So the molality is given by

$$\text{Molarity} = \frac{0.166\text{ mol}}{0.125\text{ kg}} = 1.33\ m$$

Now, K_f for water is 1.86°C molal^{-1}. Substituting the values, we get

$$\Delta T_f = K_f m = (1.86°C\ m^{-1})(1.33 m) = 2.47°C$$

Hence, the solution should freeze at 2.47°C below 0°C, or at –2.47°C.

Solved Example 8-54

A 10.0 g quantity of a compound is dissolved in 100 g of water. The solution formed has a melting point of –7.14°C. Is the compound KCl, Na_2S, or $CaCl_2$?

Solution

Let the compound be Na_2S. The number of moles of Na_2S is

$$(2Na^+S^{2-})\ 10.0\text{ g } Na_2S \times \frac{1\text{ mol } Na_2S}{78.05\text{ g } Na_2S} = 0.128\text{ mol } Na_2S$$

Therefore, the depression in freezing point is

$$\Delta T_f = 1.86 \times \frac{0.128\text{ mol}}{100\text{ g}} \times 3\text{ mol ions/mol } Na_2S = 7.14°C$$

which is same as the one given in the question, so the compound is Na_2S.

Solved Example 8-55

A solution made by dissolving 5.65 g of an unknown molecular compound in 110.0 g of benzene froze at 4.39°C. What is the molar mass of the solute?

Solution

We can use the value of ΔT_f (the difference between the freezing point of pure benzene and that of the solution) along with the value of K_f for benzene from Table 8.5 to calculate the molality of the solution. This gives the ratio of moles of solute to kilograms of benzene, which we can then use as a conversion factor to calculate the number of moles dissolved in the 110.0 g of benzene.

The freezing point of benzene is 278.5 K and that the value of K_f for benzene is 5.12 K kg mol^{-1}. The amount of freezing point depression is

$$\Delta T_f = 278.5\,\text{K} - 277.39\,\text{K} = 1.01\,\text{K}$$

We now use $\Delta T_f = K_f\, m$ to find the molality of the solution.

$$m = \frac{\Delta T_f}{K_f} = \frac{1.01\ \text{K}}{5.12\ \text{K kg mol}^{-1}} = 0.197\ \text{mol kg}^{-1}$$

This means that for every kilogram of benzene in the solution, there are 0.197 mol of solute. But we have only 110.0 g or 0.1100 kg of benzene. So the actual number of moles of solute in the given solution is found by

$$0.1100\ \text{kg benzene} \times \frac{0.197\ \text{mol solute}}{1\ \text{kg benzene}} = 0.0217\ \text{mol solute}$$

We can now obtain the molar mass. There are 5.65 g of solute per 0.0217 mol of solute:

$$\frac{5.65\ \text{g}}{0.0217\ \text{mol}^{-1}} = 260.36\ \text{g mol}^{-1}$$

The mass of one mole of the solute is 260.36 g. That is, molar mass of the solute = 260.36 g mol^{-1}.

Solved Example 8-56

A solution made by dissolving 3.46 g of an unknown compound in 85.0 g of benzene froze at 4.13°C. What is the molar mass of the compound? ($K_f = 1.86$°C molal $^{-1}$)

Solution

It is first necessary to obtain the values of the freezing point of pure benzene and the value of K_f for benzene from Table 8.5 of the text. We proceed to determine the number of moles of solute that are present and that have caused this depression in the freezing point: $\Delta T = K_f m$. Therefore,

$$m = \frac{\Delta T_f}{K_f} = \frac{5.45 - 4.13}{5.07} = 0.260\ \text{molal}$$

Next, use this molality to determine the number of moles of solute that must be present:

0.260 mol solute/kg solvent × 0.0850 kg solvent = 0.0221 mol solute

Last, determine the formula mass of the solute: 3.46 g/0.0221 mol = 157 g mol^{-1}.

Solved Example 8-57

A mixture is prepared that is 5.0% (*w*/*w*) of an unknown substance mixed with naphthalene (molar mass 128.2 g mol^{-1}). The freezing point of the mixture is found to be 77.3°C. What is the molar mass of the unknown substance? (The melting point of naphthalene is 80.2°C and $K_f = 6.9$°C molal^{-1}.)

Solution

To find the molar mass of the substance, first, we need to find the molality of the solution from the freezing point depression, and then using the 5.0% (*w*/*w*) amount, determine the moles of the solute.

$$m = \frac{\Delta T}{K_f} = \frac{80.2 - 77.3}{6.9} = 0.42\ \text{molal}$$

Assume there is 100 g of solution:

5.0% (*w*/*w*) means

$$\frac{5\ \text{g unknown substance}}{5\ \text{g unknown substance} + 95\ \text{g naphthalene}}$$

We have 95 g of naphthalene or 0.095 kg naphthalene and 5 g of the unknown.

Using the equation for molality, we can determine the number of moles of the unknown

mol unknown = (m solution)(kg solvent) = (0.420 mol kg^{-1}) (0.095 kg naphthalene) = 0.0399 mol unknown

$$\text{Hence, molar mass} = \frac{5.0 \text{ g unknown}}{0.0399 \text{ mol unknown}} = 125 \text{ g mol}^{-1}$$

Osmotic Pressure

In living things, membranes of various kinds keep mixtures and solutions organized and separated. These membranes must have a selective *permeability*. They must keep some substances from going through while letting others pass. Such membranes are said to be *semipermeable*. The degree of permeability varies with the kind of membrane. Cellophane, for example, is permeable to water and small solute particles – ions or molecules – but impermeable to very large molecules, like those of starch or proteins. Special membranes can even be prepared that are permeable only to water, not to any solutes.

Depending on the kind of membrane separating solutions of different concentration, two similar phenomena, *dialysis* and *osmosis*, can be observed. Both are functions of the relative populations of the particles of the dissolved materials, so they are colligative properties.

1. When a membrane is able to let both water and *small* solute particles through, such as the membranes in living systems, the process is called dialysis, and the membrane is called a *dialyzing membrane*. It does not permit huge molecules through, like those of proteins and starch. Artificial kidney machines use dialyzing membranes to help remove the smaller molecules of wastes from the blood while letting the blood retain its large protein molecules.
2. When a semipermeable membrane will let only solvent molecules get through, this movement is called *osmosis*, and the special membrane needed to observe it is called an osmotic membrane Figure. 8.24.

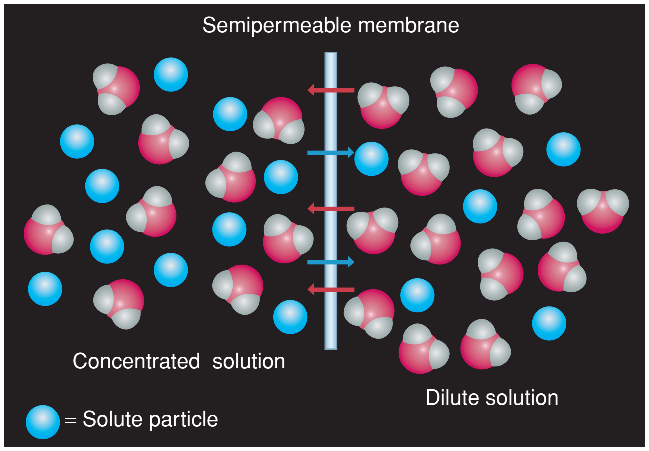


Figure 8.24 Semipermeable membrane.

Osmosis *is the tendency for a solvent to move through a thin porous membrane from a dilute solution to a more concentrated solution*. The membrane is said to be *semipermeable*, which means that small solvent molecules can pass through but large hydrated solute species cannot. Figure. 8.25 illustrates osmosis.

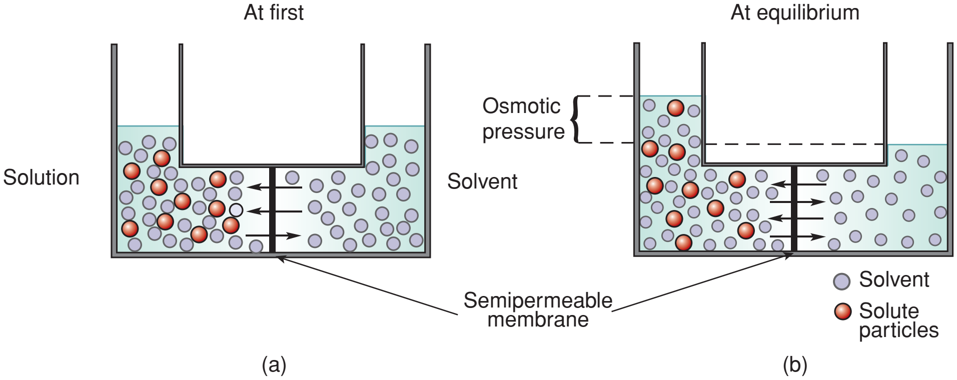


Figure 8.25 Osmotic pressure: (a) Beginning of movement of solvent molecules. (b) After the equilibrium is established and the osmotic pressure is final.

On the right is a pure solvent and on the left, a solution. The two are separated by a semipermeable membrane. Solvent molecules can pass through the membrane in both directions, but the rate at which they diffuse to the right is lower because some of the water molecules on the left are held back by solute–solvent interactions. As a result of the uneven passage of water molecules, the water level rises on the left and drops on the right. This creates increased pressure on the left, which eventually counteracts the osmosis, and equilibrium is established. *The extra pressure required to establish this equilibrium is known as the* **osmotic pressure**.

The osmotic pressure of a solution can be measured by determining the amount of counter pressure needed to prevent osmosis; this pressure can be very large. The difference between the applied pressure and atmospheric pressure is the **osmotic pressure**. On one side of the tube, there is osmotic pressure and on the left there are atmospheric + osmotic pressures. When pressure greater than the osmotic pressure is applied to a system, the flow of water can be reversed from that of osmosis. This process can be used to obtain useful drinking water from seawater and is known as **reverse osmosis**. Osmotic pressure is a colligative property and is dependent only on the concentration of the solute particles and is independent of their nature.

We observe an effect similar to osmosis if two solutions with unequal concentrations of a non-volatile solute are placed in a sealed container (Fig. 8.26). The rate of evaporation from the more dilute solution is greater than that of the more concentrated solution, but the rate of return to each is the same because both solutions are in contact with the same gas phase. As a result, neither solution is in equilibrium with the vapor. In the dilute solution, molecules of solvent are evaporating faster than they are condensing. But in the concentrated solution, just the opposite occurs; more water molecules return to the solution than leave it. Therefore, over time there is a gradual net transfer of solvent from the dilute solution to the more concentrated one until they both achieve the same concentration. Because the two solutions have unequal vapor pressures, there is a gradual net transfer of solvent from the more dilute solution into the more concentrated solution.

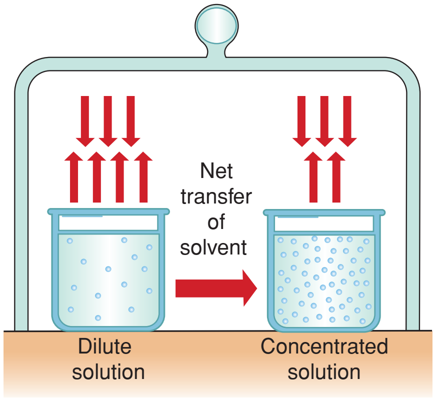


Figure 8.26 Principles at work in osmosis.

The symbol for osmotic pressure is the Greek capital pi, Π. In a dilute aqueous solution, Π is proportional both to temperature, T, and molar concentration of the solute in the solution, C:

$$\Pi \propto CT$$

The proportionality constant turns out to be the gas constant, R, so for a *dilute* aqueous solution we can write

$$\Pi = CRT \tag{8.39}$$

Of course, C is the ratio mol/L, which we can write as n/V, where n is the number of moles and V is the volume in liters. If we replace C with n/V in Eq. (8.39), and rearrange terms, we have an equation for osmotic pressure identical in form to the ideal gas law.

$$\Pi V = nRT \tag{8.40}$$

Equation (8.40) is the *van't Hoff equation for osmotic pressure*.

Osmotic pressures can be measured by an instrument called an *osmometer*, illustrated and explained in Fig. 8.27. **Osmotic pressures can be very high, even in dilute solutions**. For example, the osmotic pressure of a solution containing 1 mol of solute particles in 1 kg of water is about 22.4 atm, which is about the same as the pressure exerted by 1 mol of a gas confined in a volume of 1 L at 0°C.

When solvent moves into the solution by osmosis, the level of the solution in the capillary rises. The height reached can be related to the osmotic pressure of the solution. Like other colligative properties, osmotic pressure can also be used to determine the molar mass of solute in the solvent. The osmotic pressure is given by

$$\Pi = CRT$$

Expressing molarity in terms of mole per liter, we have

$$\Pi = \frac{n_B}{V}RT$$

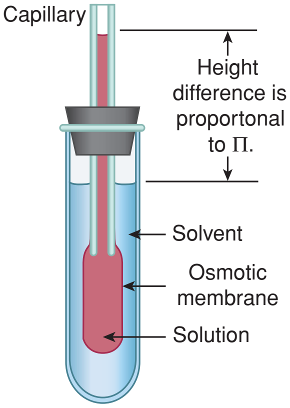


Figure 8.27 Simple osmometer.

where n_B is the number of moles of solute and V is the volume of the solution. If w_B grams of solute of molar mass M_B is dissolved in V liters of solution, the equation can be written as

$$\Pi V = \frac{w_B}{M_B} RT$$

or

$$M_B = \frac{w_B}{\Pi}\frac{RT}{V} \tag{8.41}$$

Thus mass of an unknown solute in the solution can be calculated for a solution of known concentration, by measuring the osmotic pressure.

Note: Osmotic pressure is preferred for determination of molar mass because even a small concentration of solute produces a relatively large osmotic pressure, which can be measured precisely.

Use of Osmotic Pressure in Medicine and Biology

Osmotic pressure is of tremendous importance in biology and medicine. The measurement of osmotic pressure can be very important in preparing solutions that will be used to culture tissues or to administer medicines intravenously. The concentration of solutes in the blood and other bodily fluids is important in the hydration and health of cells in our bodies. Cells are surrounded with membranes that restrict the flow of salts but allow water to pass through freely. To maintain a constant amount of water, the osmotic pressure of solutions on either side of the cell membrane must be identical.

1. **Isotonic solutions:** When the concentration of ions and other solutes in the blood or plasma is the same as that inside of a cell, the solution is said to be **isotonic**. In this case, there is no net movement of water into or out of the cell. For example, a solution that is 0.9% (w/V) NaCl has the same osmotic pressure as the contents of red blood cells, and red blood cells bathed in this solution can maintain their normal water content. The solution is said to be **isotonic** with red blood cells. Blood plasma is an isotonic solution. Intravenous solutions, such as a glucose drip or injections in a saline solution, are isotonic with the blood so as not to dilute or concentrate the solution of the cells.
2. **Hypertonic solutions:** If the concentration of solutes in the solutions around the cells is greater in the blood than in the cell, water moves out of the cell, shrinkage and dehydration occurs. The solution is called hypertonic. This process kills freshwater fish and plants that are washed out to sea.
3. **Hypotonic solutions:** If the concentration of solutes in the solutions around the cells is lower in the blood than in the cell, water moves into the cell and expands it. In either case, destruction of the cells may occur in extreme cases. A cell placed in distilled water, for example, will swell and burst. If a pair of contact lenses is rinsed with tap water instead of an isotonic saline solution, the cell damage occurs from a hypotonic solution.

The effects of isotonic, hypotonic, and hypertonic solutions on cells are shown in Fig. 8.28.

(a) In an isotonic solution (0.85% NaCl by mass), solutions on either side of the membrane have the same osmotic pressure, and there is no net flow of water across the cell membrane.

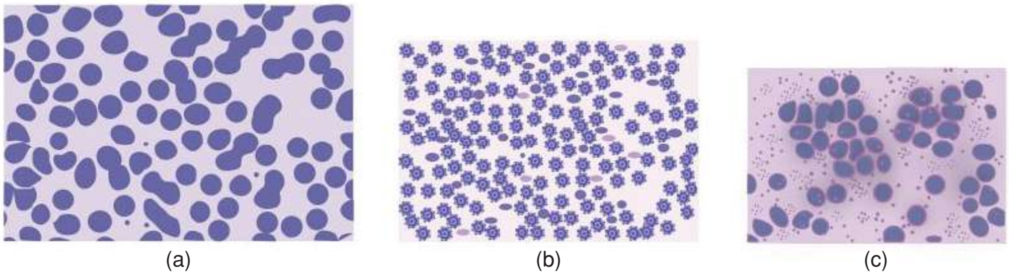

(a) (b) (c)

Figure 8.28 Effects of isotonic, hypertonic, and hypotonic solutions on red blood cells.

(b) In this hypertonic solution (5.0% NaCl by mass), water flows from areas of lower salt concentration (inside the cell) to higher concentration (the hypertonic solution), causing the cell to dehydrate.

(c) In this hypotonic solution (0.1% NaCl by mass), water flows from areas of lower salt concentration (the hypotonic solution) to higher concentration (inside the cell). The cells swell and burst.

The occurrence of osmosis can explain many natural phenomena and find many applications in everyday life. Some of them are discussed as follows:

1. People with high blood pressure are advised to have lesser intake of salt in their food. This is because the body fluids also contain Na^+ and Cl^- ions and higher intake of these would cause higher osmotic pressure. Also, it results in greater inflow of water in the cells and causes water retention in tissue cells and intercellular spaces. These results in swelling or puffiness, condition medically referred to as edema.
2. Gargling with salt water in advised in case of a sore throat. This is because by use of hypertonic salt solution, the extra water accumulated in the store throat comes out with the saline water through osmosis.
3. Meats are preserved in salt and fruits are preserved in sugar syrup to avoid bacterial infection. The cells of bacteria loose water by osmosis to the hypertonic solution and eventually die.
4. The pickled vegetables appear shriveled because they lose water to the hypertonic medium in which they are preserved.
5. Water is taken up by plants from the soil by osmotic action.

Reverse Osmosis and Water Purification

In reverse osmosis, the direction of normal osmotic flow of water across the membrane is reversed by applying pressure to the compartment with high concentration. Then, the solvent flows from the compartment containing a higher concentration of the solute to that having a lower concentration and this results in concentration of the solute in one and dilution in the other. This technique is extensively used in desalination of water. It is particularly used for making seawater fit for drinking, particularly on ships.

A schematic representation of reverse osmosis of seawater is shown in Fig. 8.29. When pressure higher than the osmotic pressure is applied to the compartment containing sea water, reverse osmosis of saline water causes water in a salt solution to move through a semipermeable membrane to the freshwater side. The pure water obtained contains minimum dissolved salts as impurities. Since the pressure required to be applied is fairly large, the semipermeable membrane selected should be able to withstand that. A variety of polymer membranes such as those made out of cellulose acetate are used for this purpose.

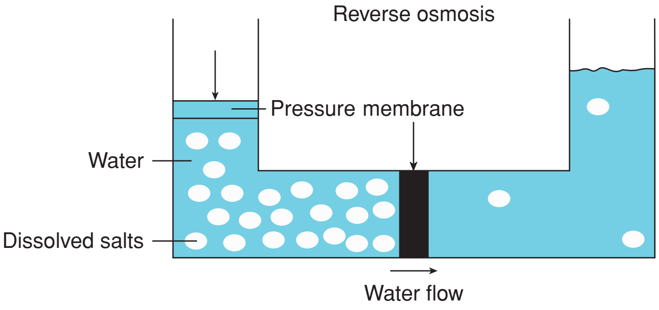


Figure 8.29 Schematic representation of desalination by reverse osmosis.

Solved Example 8-58

A very dilute solution, 0.00100 M sugar in water, is separated from pure water by an osmotic membrane. What osmotic pressure in torr develops at 25°C?

Solution

Substituting into $\Pi = CRT$, and making sure to use the temperature in kelvins so the units cancel correctly, we get

$$\begin{aligned}\Pi &= CRT\\ &= (0.00100\ \text{mol L}^{-1})(0.0821\ \text{L atm mol}^{-1}\text{K}^{-1})(298\ \text{K})\\ &= 0.0245\ \text{atm}\end{aligned}$$

In torr we have

$$\Pi = 0.0245\ \text{atm} \times \frac{760\ \text{torr}}{1\ \text{atm}} = 18.6\ \text{torr}$$

The osmotic pressure of 0.00100 *M* sugar in water is 18.6 torr.

Solved Example 8-59

Blood freezes at 272.44 K and a solution of 3.0 g of urea in 250 g of water freezes at 272.63 K. Calculate osmotic pressure of blood at 310 K. (Assume density of blood at 310 K to be 1 g cm^{-3}.)

Solution

In this question, we first calculate molality of urea solution.

$$m = \frac{3/60}{250} \times 1000 = 0.2 \text{ molal}$$

Therefore, K_f of water from urea solution is

$$K_f = \frac{\Delta T_f}{m} = \frac{273 - 272.63}{0.2} = \frac{0.37}{0.2} = 1.85 \text{ K molal}^{-1}$$

Now, we determine the molality of blood by using:

$$\Delta T_f = K_f m \Rightarrow 273 - 272.44 = 1.85 \times m$$

$$\Rightarrow m = \frac{01.56}{1.85} = 0.303 \text{ molal}$$

Colligative properties are defined for dilute solutions by assuming molarity = molality.

Therefore, molality = molarity = 0.303. Now, using $\Pi = CRT$, we get

$$\Pi = 0.303 \times 0.0821 \times 310 = 7.7 \text{ atm}$$

Solved Example 8-60

What is the osmotic pressure, in mm Hg and mm of water, of a protein solution when 5.00 g of the protein (molar mass 230,000 g mol^{-1}) is used to prepare 100.0 mL of an aqueous solution at 4.0°C? (The height of a column of liquid supported by any pressure is inversely proportional to the density of the liquid. The equivalence to use is 1 torr = 13.6 mm H_2O).

Solution

Using the equation $\Pi = CRT$, we get

$$C = \frac{(5 \text{ g protein})\left(\dfrac{1 \text{ mol protein}}{230\,000 \text{ g protein}}\right)}{0.1000 \text{ L solution}}$$

$$= 2.17 \times 10^{-4} \text{ M solution}$$

Now, $R = 0.0821$ L atm K^{-1} mol^{-1}, $T = 4.0 + 273.2 = 277.2$ K. Substituting, we get

$\Pi = (2.17 \times 10^{-4}$ M solution)(0.0821 L atm K^{-1} mol^{-1})(277.2 K) = 4.95×10^{-3} atm

$$\text{mm Hg} = 4.94 \times 10^{-3} \text{ atm} \left(\frac{760 \text{ mm Hg}}{1 \text{ atm}}\right) = 3.76 \text{ mm Hg}$$

$$\text{mm } H_2O = 3.76 \text{ mm Hg} \left(\frac{13.6 \text{ mm } H_2O}{1 \text{ mm Hg}}\right) = 51.1 \text{ mm } H_2O$$

Solved Example 8-61

An aqueous solution of glucose ($C_6H_{12}O_6$) has an osmotic pressure of 42.5 torr at 25°C. How many grams of glucose are in 125 mL of this solution?

Solution

We can use the equation $\Pi = CRT$:

$$42.5 \text{ torr}\left(\frac{1 \text{ atm}}{760 \text{ torr}}\right) = (C)(0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1})(298 \text{ K})$$

$$\Rightarrow C = 2.29 \times 10^{-3} \text{ M}$$

$$\text{Mass} = (125 \text{ mL})\left(\frac{2.29 \times 10^{-3} \text{ mol}}{1000 \text{ mL}}\right)\left(\frac{180.2 \text{ g } C_6H_{12}O_6}{1 \text{ mol } C_6H_{12}O_6}\right)$$

$$= 0.0516 \text{ g } C_6H_{12}O_6$$

Solved Example 8-62

An aqueous solution with a volume of 100 mL and containing 0.122 g of an unknown molecular compound has an osmotic pressure of 16.0 torr at 21.0°C. What is the molar mass of the solute?

Solution

First, the solution's molarity, *M*, is calculated using the osmotic pressure. The osmotic pressure in atm is

$$\Pi = 16.0\ \text{torr} \times \frac{1\ \text{atm}}{760\ \text{torr}} = 0.0211\ \text{atm}$$

The temperature, 20.1°C, corresponds to 294 K (273 + 21). Using the relation $\Pi = CRT$, we get

$$0.0211\ \text{atm} = (C)(0.0821\ \text{L atm mol}^{-1}\ \text{K}^{-1})(294\ \text{K})$$
$$\Rightarrow C = 8.74 \times 10^{-4}\ \text{mol L}^{-1}$$

Thus, 0.122 g of solute is present in 100 mL or 0.100 L of solution, not in a whole liter. So the number of moles of solute corresponding to 0.122 g is found by

$$\text{Moles of solute} = 0.100\ \text{L soln} \times \frac{8.74 \times 10^{-4}\ \text{mol}}{1\ \text{L soln}}$$
$$= 8.74 \times 10^{-5}\ \text{mol}$$

The molar mass of the solute is the number of grams of solute per mole of solute:

$$\text{Molar mass} = \frac{0.122\ \text{g}}{8.74 \times 10^{-5}\ \text{mol}} = 1.40 \times 10^{3}\ \text{g mol}^{-1}$$

Solved Example 8-63

Estimate the molecular mass of a protein when 0.137 g of the protein, dissolved in 100.0 mL of water at 4°C, supports a column of water that is 6.45 cm high. The density of mercury is 13.6 g mL^{-1}

Solution

We know that $\Pi = CRT$. The value of Π in atm is

$$\Pi = 6.45\ \text{cm water}\left(\frac{10\ \text{mm H}_2\text{O}}{1\ \text{cm H}_2\text{O}}\right)\left(\frac{1.00\ \text{g mL}^{-1}}{13.6\ \text{g mL}^{-1}}\right)$$
$$\times\left(\frac{1\ \text{atm}}{760\ \text{mm Hg}}\right) = 6.24 \times 10^{-3}\ \text{atm}$$

and R = 0.0821 L atm $\text{mol}^{-1}\ \text{K}^{-1}$, $T = 277$ K. Substituting the values, we get molarity as

$$C = \frac{\Pi}{RT} = \frac{(6.24 \times 10^{-3}\ \text{atm})}{(0.0821\ \text{L atm mol}^{-1}\text{K}^{-1}) \times (277\ \text{K})}$$
$$= 2.74 \times 10^{-3}\ \text{mol L}^{-1}$$

The number of moles of protein = $(2.74 \times 10^{-3}\ \text{mol L}^{-1})(0.1000\ \text{L}) = 2.74 \times 10^{-4}$ mol

$$\text{Therefore, molar mass} = \frac{0.137\ \text{g}}{2.74 \times 10^{-4}\ \text{mol}}$$
$$= 4.99 \times 10^{4}\ \text{g mol}^{-1}$$

8.12 | ABNORMAL MOLAR MASSES AND VAN'T HOFF FACTOR

When an ionic compound is dissolved as a solute in a solvent (water), it dissociates in ions. For example, potassium chloride dissociates to give K^+(aq) and Cl^- (aq)ions

$$\text{KCl(s)} + \text{water} \rightarrow \text{K}^+\text{(aq)} + \text{Cl}^-\text{(aq)}$$

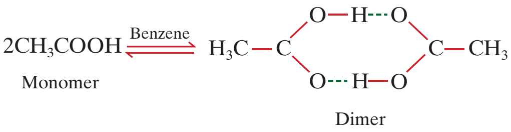
(a) If KCl were completely dissociated in water, the K^+ and Cl^- ions would be totally independent.

(b) Interionic attractions cause some ions to group together as ion pairs, which reduces the total number of independent particles in the solution.

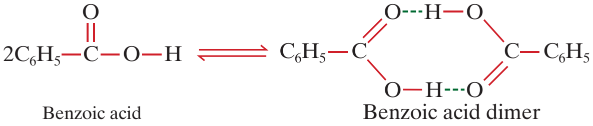
Thus, the number of particles in solution is greater than the number of particles added in the solid state. Since colligative properties depend only on the number of particles in solution and not on their nature, the observed colligative property of the solution is greater than that predicted on the basis of Raoult's law or ideal behavior. Thus the elevation in boiling point of the solution would be twice that of expected from addition of one mole of KCl and the molar mass determined would be half of the expected value. Thus, in case of a solute that dissociates in the solution, the **experimentally determined molar mass is always lower than the actual value**.

Note: As solutions of electrolytes are made more and more *dilute*, the observed and calculated freezing points come closer and closer together. At greater dilutions, the association (coming together) of ions is less a complication because the ions can be farther apart. So the solutes behave increasingly as if they were 100% separated into their ions at ever higher dilutions.

On the other hand, when a solute undergoes association on dissolving in a solvent, the number of particles of solute is reduced. As a result, the experimentally determined colligative property is lower than that expected from Raoult's law and ideal behavior. For example, the experimentally determined values of colligative properties of solution of acetic acid in benzene are lower than those calculated theoretically. This is because the molecules of acetic acid aggregate in benzene by hydrogen bonding to form dimers.



Similarly, benzoic acid also dimerizes in benzene. The molecules are held together by hydrogen bonds, indicated by the dotted lines in the following.



If we presume that all the molecules of acetic or benzoic acid are associated in the solution, then the lowering in freezing point would be half of the expected value and the molar mass determined would be twice the expected value. Thus in case of association of solute particles, the molar mass determined experimentally is always higher than the actual value. These values of molar mass that are higher or lower than the true value are known as *abnormal molar mass*.

The extent of dissociation or association of a solute in solution is expressed in terms of van't Hoff factor i. It is defined as the ratio of experimentally determined value of colligative property to the calculated value of colligative property based on the theoretical relations (Raoult's law and ideal behavior).

$$i = \frac{\text{Observed value of colligative property}}{\text{Calculated value of colligtive property}} \tag{8.42}$$

In terms of association/dissociation of solute particles, it can be expressed as

$$i = \frac{\text{Number of moles of solute after association/dissocaition}}{\text{Number of moles of solute before dissolution}}$$

In terms of molar mass obtained from colligative properties and the actual mass, it can be expressed as

$$i = \frac{\text{Normal molar mass}}{\text{Abnormal molar mass}}$$

We can conclude the following for the van't Hoff factor:

1. When the solute does not associate or dissociate in the solution, the value of van't Hoff factor $i = 1$. In this case, the observed and calculated colligative properties are the same. The values of molar mass determined by colligative properties is the same as the normal mass.
2. When the solute undergoes dissociation in solution, $i > 1$. The observed values of colligative properties are more than the calculated values and the formula mass is *less than* that obtained by measurement of colligative properties.
3. When the solute undergoes association in solution, $i < 1$. The observed values of colligative properties are less than the calculated values and the formula mass is *greater than* that obtained by measurement of colligative properties.

For solutes that associate or dissociate in solution, the equation of colligative properties needs to be modified to include the van't Hoff factor.

$$\begin{aligned}
&\text{Relative lowering of vapor pressure:} && \Delta p = \frac{p_A^\circ - p_A}{p_A^\circ} = i\frac{n_B}{n_A} \\
&\text{Elevation of boiling point:} && \Delta T_b = iK_b m \\
&\text{Depression of freezing point:} && \Delta T_f = iK_f m \\
&\text{Osmotic pressure:} && \Pi = i\frac{n_B}{V}RT
\end{aligned} \qquad (8.43)$$

The hypothetical van't Hoff factor, *i*, is 2 for NaCl, KCl and $MgSO_4$, which break up into two ions on 100% dissociation. For K_2SO_4, the theoretical value of *i* is 3 because one K_2SO_4 unit gives three ions. The actual van't Hoff factors for several electrolytes at different dilutions are given in Table 8.6. Notice that with decreasing concentration (i.e., at higher dilutions) the experimental van't Hoff factors agree better with their corresponding hypothetical van't Hoff factors.

The increase in the percentage dissociation that comes with greater dilution is not the same for all salts. In going from concentrations of 0.1 to 0.001 molal, the increase in percentage dissociation of KCl, as measured by the change in *i*, is only about 7%. But for K_2SO_4, the increase for the same dilution is about 22%, a difference caused by the anion, SO_4^{2-}. It has twice the charge as the anion in KCl and so the SO_4^{2-} ion attracts K^+ more strongly than can Cl^-. Hence, making an ion of 2– charge and an ion of 1+ charge farther apart by dilution has a greater effect on their acting independently than giving ions of 1– and 1+ charge more room. When *both* cation and anion are doubly charged, the improvement in percent dissociation with dilution is even greater. We can see from Table 8.6 that there is an almost 50% increase in the value of *i* for $MgSO_4$ as we go from a 0.1 to a 0.001 molal solution.

Table 8.6 van't Hoff factors vs. concentration

	van't Hoff factor, *i*			
Compound	Molal concentration ($mol_{salt}\ kg_{water}^{-1}$)			Value of *i* if 100% dissociation occurred
Salt	0.1	0.01	0.001	–
NaCl	1.87	1.94	1.97	2.00
KCl	1.85	1.94	1.98	2.00
K_2SO_4	2.32	2.70	2.84	3.00
$MgSO_4$	1.21	1.53	1.82	2.00

Solved Example 8-64

Following are equimolal aqueous solutions: 1 molal urea, 1 molal KCl, 1 molal $MgCl_2$ and 1 molal Na_3PO_4. Arrange them in increasing **(a)** boiling point, **(b)** freezing point, **(c)** osmotic pressure, **(d)** vapor pressure.

Solution

For dilute solutions, we assume molality = molarity. Now, *i* for urea, KCl, $MgCl_2$ and Na_3PO_4 are 0, 2, 3 and 4, respectively.

(a) **Boiling point of solution:** From the expression $\Delta T_b = i\,K_b\,m$, we have that the greater the value of *i*, greater is the value of ΔT_b and boiling point of solution. Therefore, the order is

1 molal urea < 1 molal KCl < 1 molal $MgCl_2$ < 1 molal Na_3PO_4

(b) **Freezing point of solution:** From the expression $\Delta T_f = i\,K_f\,m$, we have that the greater the value of *i*, greater is the value of ΔT_f but smaller is the freezing point of solution. Therefore, the order is

1 molal Na_3PO_4 < 1 molal $MgCl_2$ < 1 molal KCl > <1 molal urea

(c) **Osmotic pressure (Π):** From the expression $\Pi = i\,CRT$, we have that the greater the value of *i*, greater is the osmotic pressure of solution. Therefore, the order is

1 molal urea < 1 molal KCl < 1 molal $MgCl_2$ < 1 molal Na_3PO_4.

(d) Vapor pressure of solution: From the expression $\Delta p/p^\circ = i\,x_B = i\,(n_B/n_A + n_B) \approx i(n_B/n_A)$, we have that the greater the value of i, greater is the value of Δp but smaller the vapor pressure of the solution. Therefore, the order is

1 molal Na_3PO_4 < 1 molal $MgCl_2$ < 1 molal KCl > < 1 molal urea

Solved Example 8-65

Which of the following 0.1 M aqueous solution will have the lowest freezing point: potassium sulphate, sodium chloride, urea and glucose. **(IIT-JEE 1989)**

Solution

We know that $\Delta T_f = i \times K_f \times m$. Since i value of K_2SO_4 is highest (i = 3), so the depression freezing point is maximum, and hence freezing point is minimum.

Solved Example 8-66

The freezing point of equimolal aqueous solution will be highest for which solution and why?
$C_6H_5NH_3Cl$ (aniline hydrochloride), $Ca(NO_3)_3$, $La(NO_3)_3$, $C_6H_{12}O_6$ (glucose) **(IIT-JEE 1990)**

Solution

As i is greatest for glucose, hence from the expression $\Delta T_f = i \times K_f \times m$, the freezing point will be highest for $C_6H_{12}O_6$ (glucose).

Solved Example 8-67

0.2 molal acid HX is 20% ionized in solution. K_f = 1.86K molal^{-1} then calculate the freezing point of the solution. **(IIT-JEE 1995)**

Solution

The reaction involved is

$$\begin{array}{lccc} & HX & \rightleftharpoons & H^+ + X^- \\ \text{Initial moles} & 1 & & 0 \quad 0 \\ \text{Moles at equilibrium} & 1-0.2 & & 0.2 \quad 0.2 \end{array}$$

Total number of moles at equilibrium = 0.8 + 0.2 + 0.2 = 1.2 = i

Therefore, depression in freezing point is

$$\Delta T_f = i \times K_f \times m = 1.2 \times 1.86 \times 0.2 = 0.45^\circ\text{C}$$

So, the freezing point, $T_f = 0 - 0.45 = -0.45^\circ$C.

Solved Example 8-68

The molecular weight of benzoic acid in benzene as determined, by depression in freezing point method corresponds to which property of benzoic acid? **(IIT-JEE 1996)**

Solution

Dimerization of benzoic acid takes place as follows in non-polar solvent:

$$2C_6H_5COOH \rightleftharpoons (C_6H_5COOH)_2$$

Therefore, M_{obs} and M_{expt} can be calculated and related.

Solved Example 8-69

Estimate the freezing point of aqueous 0.106 molal $MgCl_2$, assuming that it dissociates completely.

Solution

$MgCl_2$ is an ionic compound that dissociates in water as

$$\begin{array}{rccc} & MgCl_2(s) \rightarrow & Mg^{2+}(aq) + & 2Cl^-(aq) \\ \text{Initial moles} & 1 & 0 & 0 \\ \text{Moles at equilibrium} & 1-x & x & 2x \end{array}$$

Total number of moles at equilibrium = $1 - \alpha + \alpha + 2\alpha = 1 + 2\alpha$. The van't Hoff factor is $(1 + 2\alpha)/1$. Now, assuming 100% dissociation, we get $i = 1 + 2 = 3$. Substituting in the equation $\Delta T_f = iK_f m$, where K_f for water is 1.86°C $molal^{-1}$, we get

$$\Delta T_f = 3 \times (1.86°C\ molal^{-1})(0.106\ molal) = 0.591°C$$

The freezing point is depressed below 0.000°C by 0.591°C, so we calculate that this solution freezes at –0.591°C.

Solved Example 8-70

Calculate the freezing point of aqueous 0.237 molal LiCl on the assumption that it is 100% dissociated. Calculate what its freezing point would be if the percent dissociation were 0%.

Solution

For the solution as if the solute were 100% dissociated:

$\Delta T_f = (1.86°C\ molal^{-1})(2 \times 0.237\ molal) = 0.882°C$ and the freezing point should be –0.882°C.

For the solution as if the solute were 0% dissociated, we have

$\Delta T_f = (1.86°C\ molal^{-1})(1 \times 0.237\ molal) = 0.441°C$ and the freezing point should be –0.441°C.

Solved Example 8-71

Determine the freezing point depression of aqueous solutions of $MgSO_4$ that are **(a)** 0.1 molal, **(b)** 0.01 molal and **(c)** 0.001 molal. Which of these could be measured with a laboratory thermometer that has markings at 1°C intervals?

Solution

We use the freezing point depression equation: $\Delta T_f = K_f m$. Remember that there are two moles of ions for each mole of $MgSO_4$. The K_f water = 1.86°C $molal^{-1}$

(a) For 0.1 molal $MgSO_4$, $m = 0.2$ molal. Therefore, $\Delta T_f = (1.86°C\ molal^{-1})(0.2\ molal) = 0.372°C$.

(b) For 0.01 molal $MgSO_4$, $m = 0.02$ molal. Therefore, $\Delta T_f = (1.86°C\ molal^{-1})(0.02\ molal) = 0.0372°C$.

(c) For 0.001 molal $MgSO_4$, $m = 0.002$ molal. Therefore, $\Delta T_f = (1.86°C\ molal^{-1})(0.002\ molal) = 0.00372°C$.

The first freezing point depression could be measured using a laboratory thermometer that can measure 0.1°C increments.

Solved Example 8-72

1.22 g of benzoic acid is dissolved in 100 g of acetone and 100 g of benzene separately. Boiling point of the solution in acetone increases by 0.17°C, while that in the benzene increases by 0.13°C; K_b for acetone and benzene is 1.7 K kg mol^{-1} and 2.6 K kg mol^{-1}, Find molecular weight of benzoic acid in two cases and justify your answer.

(IIT-JEE 2004)

Solution

Given that 1 kg acetone (K_b = 1.7 K kg mol^{-1}), 1 kg benzene (K_b = 2.6 A K kg mol^{-1}), $w_{benzoic} = 1.22$ g, $w_{acetone} = 100$ g, $w_{benzene} = 100$ g, $\Delta T_{b(acetone)} = 0.17°C$ and $\Delta T_{b(benzene)} = 0.13°C$.

We use the expression

$$\Delta T_b = \frac{1000 K_b \times w_B}{w_A \times M_B}$$

where $w_B = w_{\text{benzoic}} = 1.22$ g, M_B is molecular weight of benzoic acid and $w_A = w_{\text{acetone}}$ or w_{benzene}. Hence, substituting the values, we get

For acetone solution: $M_B = \dfrac{1000 \times 1.7 \times 1.22}{0.17 \times 100} = 122\ \text{g mol}^{-1}$

For benzene solution: $M_B = \dfrac{1000 \times 2.6 \times 1.22}{0.13 \times 100} = 244\ \text{g mol}^{-1}$

Molecular weight of C_6H_5COOH is 122 and thus it is evident that benzoic acid remains as normal molecular species in acetone but shows 100% dimerization in C_6H_6, that is, in C_6H_6 it exists as $(C_6H_5COOH)_2$.

Solved Example 8-73

The degree of dissociation of $Ca(NO_3)_2$ in a dilute aqueous solution, containing 7.0 g of the salt per 100 g water at 100°C is 70%. If the vapor pressure of water at 100°C is 760 mm Hg, calculate vapor pressure of the solution. **(IIT-JEE 1991)**

Solution

The reaction involved is

$$\begin{array}{lccc} & Ca(NO_3)_2 & \rightleftharpoons Ca^{2+} & + 2NO_3^{2-} \\ \text{Initial moles} & 1 & 0 & 0 \\ \text{Moles at equilibrium} & 1-\alpha & \alpha & 2\alpha \end{array}$$

Total number of moles at equilibrium = $1 - \alpha + \alpha + 2\alpha$ $\Rightarrow i = 1 + 2\alpha = 1 + 2(0.7) = 2.4$

According to Raoult's law,

$$\frac{p^\circ - p_s}{p^\circ} = x_A = \frac{n_A}{n_A + n_B} \qquad (1)$$

Given that $p^\circ = 760$ mm Hg, $n_A = w_A/M_A = 7/164$, $n_B = w_B/M_B = 100/18$. However, due to abnormal molar mass, the molar mass calculated for $Ca(NO_3)_2$ is

$$\frac{M_{\text{obs}}}{M_{\text{calc}}} = 1 + 2\alpha \Rightarrow M_{\text{calc}} = \frac{164}{2.4} = 68.33\ \text{g mol}^{-1}$$

Therefore, $n_A = w_A/M_A = 7/68.33$. Substituting values in Eq. (1), we get

$$\frac{p^\circ - p_s}{p_s} = \frac{7 \times 18}{68.33 \times 100} = 0.0184$$

or $$p_s = \frac{760}{1.0184} = 746.26\ \text{mm Hg}$$

Solved Example 8-74

Calculate the density of glycol solution whose 5.8 L on addition to 10 L of water produces a solution which protects automobile radiator down to −20°C. Calculate the temp at which this solution boils. (K_b and K_f for water = 1.86 and 0.52°C molal^{-1}, respectively).

Solution

We know that mass of glycol = density × volume = $\rho \times 5.8$. Therefore,

$$\text{Moles of glycol} = \frac{\rho \times 5.8}{62} \qquad (1)$$

$$\text{Therefore, } \Delta T_f = iK_f \times m = 1 \times 1.86 \times \frac{\text{Moles of glycol}}{10} \qquad (2)$$

From Eqs. (1) and (2), we get

$$\Delta T_f = iK_f \times m = 1 \times 1.86 \times \frac{\rho \times 5.8}{62} \times \frac{1}{10}$$

$$\Rightarrow 20 = \frac{1.86}{10} \times \frac{\rho \times 5.8}{62} \Rightarrow \rho = 1149.4\ \text{g L}^{-1}$$

$$\text{Therefore, } \Delta T_b = \frac{\rho \times 5.8}{62} \times \frac{0.52}{10} = 5.59°\text{C}$$

So, the new boiling point = 100 + 5.59 = 105.6°C.

Solved Example 8-75

To 500 cm^3 of water, 3×10^{-3} kg of acetic acid is added. If 23% of acetic acid is dissociated, what will be the depression in freezing point? (K_f and density of water are 1.86 K kg mol^{-1} and 0.997 g cm^{-3}, respectively.) **(IIT-JEE 2000)**

Solution

The reaction involved is

$$\begin{array}{lccc} & CH_3COOH & \rightleftharpoons CH_3COO^- & + H^+ \\ \text{Initial moles} & 1 & 0 & 0 \\ \text{Moles at equilibrium} & 1-\alpha & \alpha & \alpha \end{array}$$

Total number of moles at equilibrium $= 1-\alpha+\alpha+\alpha \Rightarrow$ $i = 1+\alpha = 1+0.23 = 1.23$.

Hence,

$$\Delta T_\text{f} = iK_\text{f} \times m = \frac{1.23 \times 1.86 \times 3 \times 10^{-3} \times 10^3}{\dfrac{60 \times 500 \times 0.997}{10^3}}$$

$$= 0.229°\text{C}$$

Solved Example 8-76

75.2 g of C_6H_5OH (phenol) is dissolved in a solvent of $K_\text{f} = 14°\text{C molal}^{-1}$. If the depression in freezing point is 7 K then find the percentage of phenol that dimerizes. **(IIT-JEE 2006)**

Solution

The reaction involved is

$$\begin{array}{rll} & 2C_6H_5OH \rightleftharpoons & (C_6H_5OH)_2 \\ \text{Initial moles} & 1 & 0 \\ \text{Moles at equilibrium} & 1-\alpha & \alpha/2 \end{array}$$

Total number of moles at equilibrium = $1 - \alpha + \alpha/2 \Rightarrow$ $i = 1 - \alpha/2$ (association).

Hence, $\Delta T_\text{f} = K_\text{f} \times m_\text{obs} \times i \Rightarrow \dfrac{7}{14} = \dfrac{75.2}{94} \times \left(1-\dfrac{\alpha}{2}\right)$

$$\Rightarrow \alpha = 0.75$$

So, the percentage of phenol that dimerizes = 75%.

Solved Example 8-77

Acetic acid associates in benzene to form a dimer, 1.65 g of acetic acid when dissolved in 100 g of benzene raised the boiling point by 0.36°C. Calculate the van't Hoff factor and degree of association of acetic acid. (K_b for benzene $= 2.57°\text{C molal}^{-1}$)

Solution

First, we calculate molecular mass from elevation in boiling point.

$$M_\text{B} = K_\text{b}\left(\frac{w_\text{B}}{w_\text{A}\Delta T_\text{b}} \times 1000\right) = 2.57\left(\frac{1.65}{100 \times 0.36} \times 1000\right)$$

$$= 117.8 \text{ g mol}^{-1}$$

Now, van't Hoff factor can be calculated as

$$i = \frac{\text{Calculated molecular mass}}{\text{Observed molecular mass}} = \frac{60}{117.8} = 0.509$$

The reaction involved is

$$\begin{array}{rll} & 2CH_3COOH \rightleftharpoons & (CH_3COOH)_2 \\ \text{Initial moles} & 1 & 0 \\ \text{Moles at equilibrium} & 1-\alpha & \alpha/2 \end{array}$$

Total number of moles at equilibrium = $1 - \alpha + \alpha/2 \Rightarrow$ $i = (1 - \alpha/2)/1 = 1 - \alpha/2$.

Therefore, degree of association is

$$0.509 = \frac{1-\alpha/2}{1} \Rightarrow \alpha = 0.982$$

So, the percentage of acetic acid that dimerizes = 98.2%.

Solved Example 8-78

Calculate osmotic pressure of a solution containing 0.01 mol of NaCl and 0.03 mol of glucose in 500 mL at 27°C.

Solution

The effective molarity is

$$C_\text{effective} = i_\text{NaCl}(=2) \times C_\text{NaCl} + i_\text{Glucose}(=1) \times C_\text{Glucose}$$

$$= \left(2 \times \frac{0.1}{500/1000} + 1 \times \frac{0.032}{500/1000}\right) = 0.1\text{ M}$$

Therefore, the osmotic pressure is $\Pi = C_\text{effective}RT = 0.1 \times 0.082 \times 300 = 2.46$ atm

Solved Example 8-79

1.0 g of monobasic acid when dissolved in 100 g of pure water lowers the freezing point by 0.168° C, 0.2 g of the same acid when dissolved and titrated required 15.1 mL of N/10 base. Determine the degree of dissociation of the acid. (K_f of water is 1.86 K molal^{-1}.)

Solution

Calculate the molecular mass (observed from colligative property) using the relation:

$$M_{B(obs)} = K_f\left(\frac{w_B}{w_A N \times V_1}\times 1000\right)$$
$$= 1.86\left(\frac{1}{100\times 0.168}\times 1000\right) = 110.6\,\text{g mol}^{-1}$$

Now, we calculate the actual molecular mass from neutralization experiment where mass equivalent of acid = mass equivalent of base.

$$\frac{0.2}{M/1} = 0.1\times 15.1 \Rightarrow M_{B(calc)} = 132.45\,\text{g mol}^{-1}$$

The van't Hoff factor can be calculated as

$$i = \frac{M_{B(calc)}}{M_{B(obs)}} = \frac{132.45}{110.6} = 1.19$$

The reaction involved is

$$\begin{array}{rccc} & \text{HA} & \rightleftharpoons & \text{H}^+ + \text{A}^- \\ \text{Initial moles} & 1 & & 0 \quad\; 0 \\ \text{Moles at equilibrium} & 1-\alpha & & \alpha \quad\; \alpha \end{array}$$

Total number of moles at equilibrium = 1 − α + α + α $\Rightarrow i = 1 + \alpha$.

Therefore, the degree of dissociation is $\alpha = 1 - 1.19 =$ 0.19 or 19%.

Solved Example 8-80

The freezing point of an aqueous saturated solution of I_2 is – 0.0024°C. More than this can dissolve in a KI solution because of the following equilibrium

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq)$$

0.1 M KI solution dissolves 12.5 g L^{-1} of I_2. Calculate the equilibrium constant K_C for the above equilibrium. Also calculate the freezing point of the resulting solution. Assume molarity to be equal to molality and also assume that concentration of I in all saturated solutions is same. (K_f of water is 1.86 K molal^{-1}.)

Solution

We know that $\Delta T_f = K_f m$. Therefore,

$$m = \frac{0.0024}{1.86} = 0.0013\,\text{mol kg}^{-1}$$

or molarity = 0.0013 mol L^{-1} (in case of solvent water molarity = molality).

The reaction involved is

$$\begin{array}{rcccc} & I_2(aq) & + & I^-(aq) \rightleftharpoons & I_3^-(aq) \\ \text{Initial moles} & 0.0492 & & 0.1 & 0 \\ \text{Moles at equilibrium} & 0.0492 - x & & 0.1 - x & x \end{array}$$

Total number of moles at equilibrium $= 0.0492 - x + 0.1 - x + x = 0.1492 - x$.

Now, $0.1492 - x = 0.0013$ because of conc. of I_2 in all saturated solutions is same, so $x = 0.0479$.

Hence, the equilibrium constant is

$$K_C = \frac{[I_3^-]}{[I_2][I^-]} = \frac{0.0479}{0.0013\times 0.0521} = 707.2$$

The depression in freezing point becomes

$$\Delta T_f = 1.86(0.0479 + 0.0013 + 0.0521 + 0.1) = 0.3744\text{ K}$$

Therefore, the freezing point of the resulting solution = 272.6256 K.

SOLVED OBJECTIVE QUESTIONS FROM PREVIOUS YEAR PAPERS

1. During depression of freezing point in a solution the following are in equilibrium **(IIT-JEE 2003)**
(A) liquid solvent, solid solvent.
(B) liquid solvent solid solute.
(C) liquid solute, solid solute.
(D) liquid solute, solid solvent.

Solution

(A) On freezing a solution, only pure solvent freeze, out but the solute does not.

2. Negative deviation from ideal behavior is due to the fact that
(A) there exist molecular interaction and $pV/nRT > 1$.
(B) there exist molecular interactions and $pV/nRT < 1$.
(C) atoms have finite size and $pV/nRT > 1$.
(D) atoms have finite size and $pV/nRT < 1$.
(IIT-JEE 2003)

Solution

(B) For positive deviation, $pV = nRT + npb$
Thus, the factor npb is responsible for increasing the pV value above ideal value. Here, b is actually the effective volume of molecule. So, it is the finite size of molecules that leads to the origin of b and hence positive deviation at high pressure.

3. 0.004 M Na_2SO_4 is isotonic with 0.01 M glucose. The degree of dissociation of Na_2SO_4 is
(A) 75% (B) 50%
(C) 25% (D) 85% **(IIT-JEE 2004)**

Solution

(A) We know that $\Pi(Na_2SO_4) = iCRT = i(0.004)RT$ and $\Pi(\text{glucose}) = CRT = 0.010\ RT$. As the solutions are isotonic, which means they have same osmotic pressure, we have

$$i(0.004)RT = 0.01\ RT$$

Solving, we get $i = 2.5$. Now, consider the reaction

$$\begin{array}{lccc} & Na_2SO_4 \rightleftharpoons & 2Na^+ + & SO_4^{2-} \\ \text{Initial moles} & 1 & 0 & 0 \\ \text{Moles at equilibrium} & 1-\alpha & 2\alpha & \alpha \end{array}$$

Total number of moles at equilibrium $= 1 - \alpha + 2\alpha + \alpha \Rightarrow i = 1 + 2\alpha$.
Therefore, $\alpha = (i - 1)/2 = (2.5 - 1)/2 = 0.75$. So, the degree of dissociation is 75%.

4. The elevation in boiling point when 20.16 g of freshly prepared $CuCI_2$ (relative molar mass: 134.4 g mol^{-1}) is dissolved in 1 kg of water ($K_b = 0.52$ kg K mol^{-1}) is
(A) 0.075°C (B) 0.150°C
(C) 0.234°C (D) 0.468°C **(IIT-JEE 2005)**

Solution

(C) $$T_b = i \times K_b \times m = 3 \times 0.52 \times \left(\frac{20.16}{134.4} \times \frac{1000}{1000}\right)$$
$$= \frac{31.4496}{134.4} = 0.234°\text{C}$$

5. The elevation in boiling point of a solution of 13.44 g of $CuCl_2$ in 1 kg of water using the following information will be (mol. wt. of $CuCl_2$ = 134.4 g mol^{-1} and K_b = 0.52 K molal^{-1}.)
(A) 0.16°C (B) 0.05°C
(C) 0.1°C (D) 0.2°C **(IIT-JEE 2005)**

Solution

(A) The reaction involved is

$$\begin{array}{lccc} & CuCl_2 \rightleftharpoons & Cu^{2+} + & 2Cl^- \\ \text{Initial moles} & 1 & 0 & 0 \\ \text{Moles at equilibrium} & 1-\alpha & \alpha & 2\alpha \end{array}$$

Total number of moles at equilibrium $= 1 - \alpha + \alpha + 2\alpha \Rightarrow i = 1 + 2\alpha = 3$ (assuming $a = 100\%$).

$$\text{Therefore, } \Delta T_b = i \times K_b \times m = 3 \times 0.52 \times \frac{13.44/134.4}{1}$$
$$= 0.16°\text{C}$$

6. When 20 g of naphothoic acid ($C_{11}H_8O_{12}$) is dissolved in 50 g of benzene (K_f = 1.72 K kg mol^{-1}), a freezing point depression of 2 K is observed. The van't Hoff factor (i) is
(IIT-JEE 2007)
(A) 0.5 (B) 1
(C) 2 (D) 3

Solution

(A) Molality can be calculated using given values as

$$m = \frac{w_A}{M_A \times w_B} \times 1000 = \frac{20}{172 \times 50} \times 1000$$

Therefore, $\Delta T_f = i \times K_f \times m$
$$\Rightarrow 2 = i \times 1.72 \times \frac{20}{172 \times 50} \times 1000 \Rightarrow i = 5$$

7. Read the following paragraph and answer the questions that follow:
***Paragraph for Questions 7a to 7c*:** Properties, such as boiling point, freezing point, and vapor pressure of a pure solvent change when solute molecules are added to get homogeneous solution. These are called colligative properties. Applications of colligative properties are very useful in day-to-day life. One of its examples is the use of ethylene glycol and water mixture as antifreezing liquid in the radiator of automobiles.

A solution M is prepared by mixing ethanol and water. The mole fraction of ethanol in the mixture is 0.9. Given that:
Freezing point depression constant of water $(K_f) = 1.86$ K molal^{-1} and of ethanol $(K_f) = 2.0$ K molal^{-1}.
Standard boiling point of water = 373 K and of ethanol = 351.5 K.
Boiling point elevation constant of water $(K_b) = 0.52$ K molal^{-1} and of ethanol $(K_b) = 1.2$ K molal^{-1}.
Vapor pressure of pure water = 32.8 mm Hg and of pure ethanol = 40 mm Hg.
Standard freezing point of water = 273 K and of ethanol = 155.7 K.
Molar mass of water = 18 g mol^{-1} and of ethanol = 46 g mol^{-1}.
In answering the following questions, consider the solutions to be ideal dilute solutions and solutes to be non-volatile and non-dissociative. **(IIT-JEE 2008)**

7a. The freezing point of the solution M is

(A) 268.7 K	(B) 268.5 K
(C) 234.2 K	(D) 150.9 K

7b. The vapor pressure of the solution M is

(A) 39.3 mm Hg	(B) 36.0 mm Hg
(C) 29.5 mm Hg	(D) 28.8 mm Hg

7c. Water is added to the solution M such that the mole fraction of water in the solution becomes 0.9. The boiling point of this solution is

(A) 380.4 K	(B) 376.2 K
(C) 375.5 K	(D) 354.7 K

Solution

7a: (D) $\Delta T_f = K_f \times m = 2 \times 0.1 \times 1000/(0.9 \times 46) = 4.83$ K
Freezing point of solution = Freezing point of pure solvent – $\Delta T_f = (155.7 - 4.83) = 150.9$ K.

7b: (A) Vapor pressure of water = mole fraction of water × p° water $= 0.1 \times 32.8$ mm Hg $= 3.28$ mm Hg
Vapor pressure of ethanol = mole fraction of ethanol × p° ethanol $= 0.9 \times 40$ mm Hg $= 36$ mm Hg
Total vapor pressure of solution = 3.28 + 36 = 39.28 mm Hg

7c: (B) $\Delta T_b = K_b \times m = 0.52 \times 0.1 \times 1000/(0.9 \times 18) = 3.2$ K
Boiling point of solution = ΔT_b + boiling point of pure solvent = 373 + 3.2 = 376.2 K.

8. The Henry's law constant for the solubility of N_2 gas in water at 298 K is 1.0×10^5 atm. The mole fraction of N_2 in air is 0.8. The number of moles of N_2 from air dissolved in 10 mol of water at 298 K and 5 atm pressure is **(IIT-JEE 2009)**

(A) 4.0×10^{-4}	(B) 4.0×10^{-5}
(C) 5.0×10^{-4}	(D) 4.0×10^{-6}

Solution

(A) From Henry's law, we have

$$p = K_H x_{N_2} \Rightarrow 0.8 \times 5 = 1 \times 10^5 x_{N_2}$$
$$\Rightarrow x_{N_2} = 4 \times 10^{-5} \quad \text{(in 10 mol of water)}$$

9. Dissolving 120 g of urea (mol. wt. = 60 g mol^{-1}) in 1000 g of water gave a solution of density 1.15 g mL^{-1}. The molarity of the solution is

(A) 1.78 M	(B) 2.00 M
(C) 2.05 M	(D) 2.22 M. **(IIT-JEE 2011)**

Solution

(C) Since the solution consists of both urea and water, the mass of the solution = 1000 + 120 = 1120 g

$$\text{Volume of solution} = \frac{\text{Mass of solution}}{\text{Density of solution}} = \frac{1120}{1.15}$$
$$= 973.9 \text{ mL}$$
$$\text{Therefore, molarity} = \frac{\text{Number of moles}}{\text{Volume of solution (L)}}$$
$$= \frac{120/60}{973.9} \times 1000 = 2.05 \text{ M}$$

10. The freezing point (in °C) of a solution containing 0.1 g of $K_3[Fe(CN)_6]$ (molecular weight 329 g mol^{-1}) in 100 g of water (K_f = 1.86°C molal^{-1}) is

(A) -2.3×10^{-2}	(B) -5.7×10^{-2}
(C) -5.7×10^{-2}	(D) -1.2×10^{-2}

(IIT-JEE 2011)

Solution

(A) The depression in freezing point is given by

$$\Delta T_f = iK_f m \qquad (1)$$

where i can be calculated if we consider the following reaction:

$$K_3[Fe(CN)_6] \rightarrow 3K^+ + [Fe(CN)_6]^{3-}$$

We can calculate $i = 3 + 1 = 4$. Now, from Eq. (1)

$$\Delta T_f = i \times K_f \times \frac{w_B}{M_B} \times \frac{1000}{W_A} = 4 \times 1.86 \times \frac{0.1}{329} \times \frac{1000}{100}$$
$$= 0.0226 = 2.26 \times 10^{-2} = 2.3 \times 10^{-2}\,^\circ\text{C}$$

Freezing point of the solution $= -2.3 \times 10^{-2}$°C (as freezing point of water is 0°C).

11. For a dilute solution containing 2.5 g of a non-volatile, non-electrolyte solute in 100 g of water, the elevation in boiling point at 1 atm pressure is 2°C. Assuming concentration of solute is much lower than the concentration of solvent, the vapor pressure (mm Hg) of the solution is (take K_b = 0.76 K kg mol^{-1})

(A) 724	(B) 740
(C) 736	(D) 718 **(IIT-JEE 2012)**

Solution

(A) When a non-volatile solute is added to pure solvent, there is decrease in vapor pressure. So, according to relative lowering in vapor pressure, $\dfrac{p^\circ - p_s}{p^\circ} = x_2$

where x_2 is the number of moles of solute, p° is the vapor pressure of the pure solvent and p_s is the vapor pressure of the solution. Now, x_2 is also represented as $n_2/(n_1 + n_2)$. Thus, we have

$$\frac{p^\circ - p_s}{p^\circ} = \frac{n_2}{n_1 + n_2}$$

Neglecting n_2 from the denominator, and substituting $p^\circ = 1$ atm = 760 mm Hg, we get

$$\frac{760 - p_s}{760} = \frac{2.5/M_B}{100/18} \times \frac{1000}{1000} = \frac{18}{1000} \times m \qquad (1)$$

According to elevation in boiling point, $\Delta T_b = K_b \times m \Rightarrow 2 = 0.76 \times m \Rightarrow m = 2/0.76$.
Putting this value in Eq. (1), we get

$$\frac{760 - p_s}{760} = \frac{18}{1000} \times \frac{2}{0.76}$$
$$\Rightarrow p_s = 760 - \frac{18 \times 2 \times 760}{1000 \times 0.76}$$
$$= 760 - 36 = 724 \text{ mm Hg}$$

12. 25 mL of household bleach solution was mixed with 30 mL of 0.50 M KI and 10 mL of 4 N acetic acid. In the titration of the liberated iodine, 48 mL of 0.25 N $Na_2S_2O_3$ was used to reach the end point. The molarity of the household bleach solution is

(A) 0.48 M
(B) 0.96 M
(C) 0.24 M
(D) 0.024 M **(IIT-JEE 2012)**

Solution

(C) Consider the reaction
$CaOCl_2 + 2KI \rightarrow I_2 + Ca(OH)_2 + KCl$
According to this reaction, 25 mL of $CaOCl_2$ reacts with 30 mL of KI

$$I_2 + 2Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2NaI$$

Given that 48 mL of 0.25 N $Na_2S_2O_3$ was used to reach the end point. So, the number of moles of I_2 produced = $48 \times 0.25/2 = 6$.
According to the reaction,
Number of millimoles of bleaching powder = Number of moles of $I_2 = (1/2) \times$ Number of moles of $Na_2S_2O_3 = 6$
So, the molarity of $CaOCl_2$ =

$$\frac{\text{Number of moles of bleaching powder}}{\text{Volume of solution}} = \frac{6 \text{ mmol}}{25 \text{ mL}}$$
$$= 0.24 \text{ M}$$

13. $\mathbf{MX_2}$ dissociates into $\mathbf{M^{2+}}$ and $\mathbf{X^-}$ ions in an aqueous solution, with a degree of dissociation (α) of 0.5. The ratio of the observed depression of freezing point of the aqueous solution to the value of the depression of freezing point in the absence of ionic dissociation is _____.
(JEE Advanced 2014)

Solution

(2) The reaction involved is

$$\begin{array}{lccc} & MX_2 & \rightleftharpoons M^{2+} & + 2X^- \\ \text{Initial moles} & 1 & 0 & 0 \\ \text{Moles at equilibrium} & 1-\alpha & \alpha & 2\alpha \end{array}$$

Therefore, $i = 1 - \alpha + \alpha + 2\alpha = 1 + 2\alpha$.
Given that $\alpha = 0.5$, so $i = 1 + 2 \times 0.5 = 2$

14. If the freezing point of a 0.01 molal aqueous solution of a cobalt(III) chloride-ammonia complex (which behaves as a strong electrolyte) is –0.0558 °C, the number of chloride(s) in the coordination sphere of the complex is _____.
[K_f of water –1.86 K kg mol^{-1}] **(JEE Advanced 2015)**

Solution

(1) The depression in freezing point is given by

$$\Delta T_f = K_f \times m \times i$$
$$0.0558 = 1.86 \times 0.01 \times i$$
$$i = 3$$

Therefore, one mole of complex gives three moles of ions in solution.
Hence, the complex is $[Co(NH_3)_5Cl]Cl_2$ and the number of Cl^- ions inside the coordination sphere is 1.

15. A pressure cooker reduces cooking time for food because

(A) heat is more evenly distributed in the cooking space
(B) boiling point of water involved in cooking is increased
(C) the higher pressure inside the cooker crushes the food material
(D) cooking involves chemical changes helped by a rise in temperature **(AIEEE 2003)**

Solution

(B) This is because the boiling point of water increases as the pressure increases.

16. If liquids A and B form an ideal solution,

(A) the enthalpy of mixing is zero
(B) the entropy of mixing is zero
(C) the free energy of mixing is zero
(D) the free energy as well as the entropy of mixing are each zero **(AIEEE 2003)**

Solution

(A) A solution is ideal if the sum of the partial pressures of the components of the solution equals the observed vapor pressure of the solution, i.e., if the solution obeys Raoult's law. Since there is no change in the magnitude of the attractive forces in the two compounds present, the heat change on mixing, that is, ΔH_{mix} in such solutions must be zero. In ideal solutions, the volume of the solution is the sum of the volumes of the components before mixing, that is, there is no change in volume on mixing or ΔV_{mix} is zero.

17. In a 0.2 mol aqueous solution of a weak acid HX the degree of ionization is 0.3. Taking K_f for water as 1.85, the freezing point of the solution will be nearest to

(A) –0.480°C
(B) –0.360°C
(C) –0.260°C
(D) +0.480°C **(AIEEE 2003)**

Solution

(A) Consider the reaction,

$$\underset{\substack{1 \\ 1-0.3}}{HX} \rightarrow \underset{\substack{0.3 \\ 0.3}}{H^+} + \underset{\substack{0.3 \\ 0.3}}{X^-}$$

The total number of moles after dissociation $= 1 - 0.3\alpha + 0.3\alpha + 0.3\alpha = 1 + 0.3\alpha$. If $\alpha = 1$, then number of moles $=$ 1.3. Hence, the van't Hoff factor is $i = 1.3/1 = 1.3$.

Using the expression $\Delta T_f = i \times K_f \times m$, we get

$$\Delta T_f = 1.3 \times 1.85 \times 0.2 = +0.480°\text{C}$$

or $T_f = 0°\text{C} - 0.480°\text{C} = -0.480°\text{C}$

18. Which one of the following statements is false?

(A) Raoult's law states that the vapor pressure of a components over a solution is proportional to its mole fraction.

(B) Two sucrose solutions of the same molality prepared in different solvents will have the same freezing point depression.

(C) The correct order of osmotic pressure for 0.01 M aqueous solution of each compound is $BaCl_2 > KCl > CH_3COOH >$ sucrose.

(D) The osmotic pressure $(\Pi) = MRT$, where M is the molarity of the solution **(AIEEE 2004)**

Solution

(B) Two sucrose solutions of same molality prepared in different solvents will have the same freezing point depression. This is because freezing point does not depend upon the nature of solvents used.

$$\Delta T_f = K_f \times m$$

19. Which one of the following aqueous solutions will exhibit highest boiling point? **(AIEEE 2004)**

(A) 0.01 M Na_2SO_4 (B) 0.015 M glucose

(C) 0.015 M urea (D) 0.01 M KNO_3

Solution

(A) Since, glucose and urea are non-electrolytes and the van't Hoff's factor for KNO_3 is 2 and for Na_2SO_4 it is 3.

$$KNO_3 \rightarrow K^+ + NO_3^- \quad (i = 2)$$
$$Na_2SO_4 \rightarrow 2Na^+ + SO_4^{2-} \quad (i = 2 + 1 = 3)$$

Thus, from the expression $\Delta T_b = i \times K_b \times m$ as ΔT_b 0 i, 0.01 M Na_2SO_4 will have the highest boiling point.

20. Which of the following liquid pairs shows a positive deviation from Raoult's law? **(AIEEE 2004)**

(A) Water–hydrochloric acid

(B) Acetone–chloroform

(C) Water–nitric acid

(D) Benzene–methanol

Solution

(D) Benzene–methanol. This is because the A–A and B–B interactions are much stronger than A–B interactions. So, when methanol combined with benzene the hydrogen bonding of methanol breaks and its vapor pressure increases.

21. Benzene and toluene form nearly ideal solutions. At 20°C, the vapor pressure of benzene is 75 torr and that of toluene is 22 torr. The partial vapor pressure of benzene at 20°C for a solution containing 78 g of benzene and 46 g of toluene in torr is

(A) 50 (B) 25

(C) 37.5 (D) 53.5 **(AIEEE 2005)**

Solution

(A) According to Raoult's law, we have

$$p_B = p_B^\circ \times x_B = 75 \times \frac{1}{1.5} = 50 \text{ torr.}$$

22. Equimolar solutions in the same solvent have **(AIEEE 2005)**

(A) Same boiling point but different freezing point

(B) Same freezing point but different boiling point

(C) Same boiling and same freezing points

(D) Different boiling and different freezing points

Solution

(C) This is because colligative properties depend upon number of particles.

23. 18 g of glucose $(C_6H_{12}O_6)$ is added to 178.2 g of water. The vapor pressure of water for this aqueous solution at 100°C is

(A) 759.00 torr (B) 7.60 torr

(C) 76.00 torr (D) 752.40 torr **(AIEEE 2006)**

Solution

(D) According to Raoult's law,

$$\frac{p^\circ - p_s}{p_s} = \frac{n_{\text{solute}}}{n_{\text{solvent}}}$$

where p° is the initial pressure = 760 mm Hg and p_s is the vapor pressure of water for this solution. Also, the number of moles of solute and solvent are

$$n_{\text{solute}} = \frac{18}{\text{Mol. wt. of } C_6H_{12}O_6} = \frac{18}{180} \text{ and}$$

$$N = \frac{178.2}{\text{Mol. wt. of water}} = \frac{178.2}{18}$$

Substituting these values in the above equation, we get

$$\frac{760 - p_s}{p_s} = \frac{18/180}{178.2/18} = \frac{0.1}{9.9}$$

$$760 - p_s = \frac{1}{99} \times p_s \Rightarrow 760 \times 99 - p_s \times 99 = p_s$$

$$\Rightarrow p_s = \frac{760 \times 99}{100} = 752.4 \text{ mm Hg}$$

24. The density (in g mL^{-1}) of a 3.60 M sulphuric acid solution, that is, 29% H_2SO_4 (molar mass = 98 g mol^{-1}) by mass will be

(A) 1.45 (B) 1.64

(C) 1.88 (D) 1.22 **(AIEEE 2007)**

Solution

(D) Let the density of the solution be ρ. The molarity of the solution = 3.60 M (given). This means that 1 L of solution contains 3.6 mol or (3.6×98) g of H_2SO_4 (98 g mol^{-1} is the molecular mass of H_2SO_4). Since, the solution is 29% by mass which means 29 g of H_2SO_4 is present in 100 g, therefore, $100/\rho$ mL solution contains 29 g of H_2SO_4.

As volume = mass/density. Now, 1000 mL contains 3.6×98 g of H_2SO_4. Therefore,

$$\frac{100}{\rho} = \frac{29 \times 1000}{3.6 \times 98} \Rightarrow \rho = \frac{3.6 \times 98 \times 1000}{29 \times 1000} = 1.22\ \text{g L}^{-1}$$

25. A 5.25% solution of a substance is isotonic with a 1.5% solution of urea (molar mass = 60 g mol^{-1}) in the same solvent. If the densities of both the solutions are assumed to be equal to 1.0 g m^{-3}, molar mass of the substance will be

(A) 210.0 g mol^{-1} (B) 90.0 g mol^{-1}
(C) 115.0 g mol^{-1} (D) 105.0 g mol^{-1}

(AIEEE 2007)

Solution

(A) Isotonic solutions have the same osmotic pressure,

$$\Pi_1 = C_1RT = \Pi_2 = C_2RT$$

so $C_1 = C_2$. Let M be the molar mass of the substance. Now as the densities are same

$$\frac{5.25}{M} = \frac{15}{60} \Rightarrow M = 5.25 \times \frac{60}{1.5} = 210$$

26. A mixture of ethyl alcohol and propyl alcohol has a vapor pressure of 290 mm Hg at 300 K. The vapor pressure of propyl alcohol is 200 mm Hg. If the mole fraction of ethyl alcohol is 0.6, its vapor pressure (in mm Hg) at the same temperature will be

(A) 360 (B) 350
(C) 300 (D) 700 **(AIEEE 2007)**

Solution

(B) Let p' be the vapor pressure of ethyl alcohol in the mixture and p'' be the vapor pressure of propyl alcohol. Then, total pressure (p) of the mixture will be

$$p = p' \times (\text{Mole fraction})_{\text{ethyl alcohol}} + p'' \times (\text{Mole fraction})_{\text{propyl alcohol}}$$

$$290 = (p' \times 0.6) + (200 \times 0.4)$$

$$\Rightarrow p' = \frac{290 - (200 \times 0.4)}{0.6} = 350\,\text{mm Hg}$$

The vapor pressure of ethyl alcohol in the mixture is 350 mm of Hg.

27. The vapor pressure of water at 20°C is 17.5 mm Hg. If 18 g of glucose ($C_6H_{12}O_6$) is added to 178.2 g of water at 20°C, the vapor pressure of the resulting solution will be **(AIEEE 2008)**

(A) 17.675 mm Hg (B) 15.750 mm Hg
(C) 16.500 mm Hg (D) 17.325 mm Hg

Solution

(D) According to Raoult's law

$$\frac{p^\circ - p_s}{p_s} = X_{\text{solute}}$$

$$\frac{17.5 - p_s}{p_s} = \frac{0.1}{10} \Rightarrow \frac{17.5 - p_s}{p_s} = 0.01$$

Solving we get $p_s = 17.325$

28. At 80°C, the vapor pressure of pure liquid A is 520 mm Hg and that of pure liquid B is 1000 mm Hg. If a mixture solution of A and B boils at 80°C and 1 atm pressure, the amount of A in the mixture is (1 atm = 760 mm Hg) is **(AIEEE 2008)**

(A) 52 mol% (B) 34 mol%
(C) 48 mol% (D) 50 mol%

Solution

(D) According to Raoult's law

$$p_t = p_A^\circ X_A + p_B^\circ X_B \Rightarrow 760 = 520 X_A + p_B^\circ(1 - X_A) \Rightarrow X_A = 0.5$$

Thus, mole % of A = $0.5 \times 100 = 50\%$.

29. Two liquids X and Y form an ideal solution. At 300 K, vapor pressure of the solution containing 1 mol of X and 3 mol of Y is 550 mm Hg. At the same temperature, if 1 mol of Y is further added to this solution, vapor pressure of the solution increases by 10 mm Hg. Vapor pressure (in mm Hg) of X and Y in their pure states will be, respectively, **(AIEEE 2009)**

(A) 400 and 600 (B) 500 and 600
(C) 200 and 300 (D) 300 and 400

Solution

(A) Mole fraction of X and Y are

$$\text{Mole fraction of X} = \frac{1}{1+3} = \frac{1}{4}$$

$$\text{Mole fraction of Y} = \frac{3}{1+3} = \frac{3}{4}$$

Total pressure = partial pressure of X × Mole fraction of X + Partial pressure of Y × mole fraction of Y.

$$550 = \frac{p_X^\circ}{4} + \frac{3p_Y^\circ}{4} \qquad (1)$$

$$550.4 = p_X^\circ + 3p_Y^\circ$$

When one mole of Y is added then mole fraction of X becomes $1/(1+4) = 1/5$ and mole fraction of Y becomes $4/(1+4) = 4/5$. Now, the total pressure given as

$$560 = \frac{p_X^\circ}{5} + \frac{4p_Y^\circ}{5} \qquad (2)$$

$$560.5 = p_X^\circ + 4p_Y^\circ$$

Solving Eqs. (1) and (2), we get $p_X^\circ = 400\,\text{mm Hg}$ and $p_Y^\circ = 600\,\text{mm Hg}$.

30. A binary liquid solution is prepared by mixing *n*-heptane and ethanol. Which one of the following statements is correct regarding the behavior of the solution?

(A) The solution formed is an ideal solution.
(B) The solution is non-ideal, showing positive deviation from Raoult's law.
(C) The solution is non-ideal, showing negative deviation from Raoult's law.
(D) *n*-Heptane shows positive deviation while ethanol shows negative deviation from Raoult's law.

(AIEEE 2009)

Solution

(B) This is because for the liquid pair, *n*-heptane–ethanol molecular forces are lower than heptane–heptane and ethanol–ethanol molecular interaction forces.

31. If 10^{-4} dm^3 of water is introduced into a flask at 300 K, how many moles of water are in the vapor phase when equilibrium is established? (Given: Vapor pressure of H_2O at 300 K is 3170 Pa; $R = 8.314$ J K^{-1} mol^{-1}.)

(A) 1.27×10^{-3} mol
(B) 5.56×10^{-3} mol
(C) 1.53×10^{-2} mol
(D) 4.46×10^{-2} mol

(AIEEE 2010)

Solution

(A) Using ideal gas equation $pV = nRT$, we have

$$n = \frac{pV}{RT}$$
$$= 3170 \times 10^{-5}\text{atm} \times \frac{1\text{ L}}{0.0821\text{ L atm K}^{-1}\text{ mol}^{-1}} \times 300\text{ K}$$
$$= 1.27 \times 10^{-3}\text{ mol}$$

32. If sodium sulphate is considered to be completely dissociated into cations and anions in aqueous solution, the change in freezing point of water (ΔT_f) when 0.01 mol of sodium sulphate is dissolved in 1 kg of water is (Given $K_f =$ 1.86 K mol^{-1})

(A) 0.0186 K.
(B) 0.0372 K.
(C) 0.0558 K.
(D) 0.0744 K.

(AIEEE 2010)

Solution

(A) The expression for ΔT_f is

$$\Delta T_f = i \times K_f \times m$$

For the reaction $Na_2SO_4 \rightarrow 2Na^+ + SO_4^{2-}$, $i = 2 + 1 = 3$. Hence

$$\Delta T_f = 3 \times 1.86 \times (0.01/1) = 0.0558\text{ K}$$

33. On mixing, heptane and octane form an ideal solution. At 373 K, the vapor pressures of the two liquid components (heptane and octane) are 105 kPa and 45 kPa, respectively. Vapor pressure of the solution obtained by mixing of heptane and 35 g of octane will be (molar mass of heptane = 100 g mol^{-1} and of octane = 144 g mol^{-1})

(A) 144.5 kPa
(B) 72.0 kPa
(C) 36.1 kPa
(D) 96.2 kPa **(AIEEE 2010)**

Solution

(B) The number of moles of heptane = 25/100 and that of octane = 35/114. Now,

Mole fraction of heptane

$$= \frac{\text{Number of moles of heptane}}{\text{Total number of moles}}$$
$$= \frac{\left(\frac{25}{100}\right)}{\left(\frac{25}{100}\right) + \left(\frac{35}{114}\right)} = 0.45$$

Mole fraction of heptane + mole fraction of octane = 1.
So, mole fraction of octane = 1 – 0.55 = 0.45.

$$\text{Total pressure} = x_{\text{heptane}} \times p + x_{\text{octane}} \times p$$
$$(105 \times 0.45 + 45 \times 0.55) = 72.0\text{ kPa}$$

34. Ethylene glycol is used as an antifreeze in a cold climate. Mass of ethylene glycol which should be added to 4 kg of water to prevent it from freezing at –6°C will be: (K_f for water = 1.86 K kg mol^{-1}, and molar mass of ethylene glycol = 62 g mol^{-1}.)

(A) 204.30 g
(B) 400.00 g
(C) 304.60 g
(D) 804.32 g **(AIEEE 2011)**

Solution

(D) According to expression for depression in freezing point,

$$\Delta T_f = K_f \times m = K_f \times \left(\frac{w_2 \times 1000}{w_1 \times m_2}\right)$$

where w_1 and w_2 are the weights of solvent and solute, respectively, and m_2 is the mass of solute.

$$\Delta T_f = 0°\text{C} - (-6°\text{C}) = 6 = 1.86 \times \left(\frac{w_2 \times 1000}{4000 \times 62}\right)$$

On solving, $w_2 = 800$ g.

35. The degree of dissociation (α) of a weak electrolyte, A_xB_y is related to van't Hoff factor (i) by the expression

(AIEEE 2011)

(A) $\alpha = \dfrac{i-1}{x+y+1}$
(B) $\alpha = \dfrac{x+y-1}{i-1}$
(C) $\alpha = \dfrac{x+y+1}{i-1}$
(D) $\alpha = \dfrac{i-1}{(x+y-1)}$

Solution

(D) The van't Hoff factor is

$$i = 1 - \alpha + n\alpha = 1 + \alpha(n-1) \Rightarrow \alpha = \frac{i-1}{n-1}$$

For the reaction $A_xB_y \rightarrow xA^{y+} + yB^{x-}$, $n = x + y$, we have

$$\alpha = \frac{i-1}{n-1} = \frac{i-1}{x+y-1}$$

36. K_f for water is 1.86 kg mol^{-1}. If your automobile radiator holds 1.0 kg of water, how many grams of ethylene glycol ($C_2H_6O_2$) must you add to get the freezing point of solution lowered to –2.8°C?

(A) 72 g
(B) 93 g
(C) 39 g
(D) 27 g **(AIEEE 2012)**

Solution

(B) According to depression in freezing point, we have

$$\Delta T_f = K_f \times m = K_f \times \frac{w_{\text{solute}}/M_{\text{B(solute)}}}{w_{\text{solution}}} \times 1000$$

where $w_{\text{solution}} = 1000$ g, $\Delta T_f = 2.8$°C, M_B(solute) = 62 g mol^{-1}. Substituting, we get

$$2.8 = \frac{1.86 \times w_{\text{solute}} \times 1000}{62 \times 1000} \Rightarrow w_{\text{solute}} = 93\text{ g}$$

37. Consider separate solutions of 0.500 M $C_2H_5OH(aq)$, 0.100 M $Mg_3(PO_4)_2(aq)$, 0.250 M KBr(aq) and 0.125 M $Na_3PO_4(aq)$ at 25°C. Which statement is true about these solutions, assuming all salts to be strong electrolytes?

(A) They all have the same osmotic pressure.
(B) 0.100 M $Mg_3(PO_4)_2(aq)$ has the highest osmotic pressure.
(C) 0.125 M Na_3PO_4 (aq) has the highest osmotic pressure.
(D) 0.500 M C_2H_5OH (aq) has the highest osmotic pressure.

(JEE Main 2014)

Solution

(A) According to van't Hoff equation, $\Pi = iCRT$.

For 0.500 M C_2H_5OH (aq), $\Pi = 1\times 0.5\times RT = 0.5RT$

For 0.100 M $Mg_3(PO_4)_2$ (aq), $\Pi = 5\times 0.1\times RT = 0.5RT$

For 0.250 M KBr(aq), $\Pi = 2\times 0.25\times RT = 0.5RT$

and for 0.125 M Na_3PO_4 (aq), $\Pi = 4\times 0.125\times RT = 0.5RT$

So, all have the same osmotic pressure, and so they are isotonic solutions.

38. The vapor pressure of acetone at 20°C is 185 torr. When 1.2 g of a non-volatile substance was dissolved in 100 g of acetone at 20°C, its vapor pressure was 183 torr. The molar mass (g/mol) of the substance is:

(A) 64
(B) 128
(C) 488
(D) 32

(JEE Main 2015)

Solution

(A) Using the colligative property (relative lowering of vapor pressure)

$$\frac{p_0 - p_s}{p_s} = \frac{w_2 \times M_1}{M_2 \times w_1}$$

$$\frac{185-183}{183} = \frac{1.2\times 58}{M_2\times 100} \Rightarrow M_2 = 64 \text{ g mol}$$

REVIEW QUESTIONS

1. The molecules of a compound are composed of one phosphorus and multiple chlorine atoms. This gaseous compound dissolves in water to form a hydrochloric acid solution and phosphorus acid (H_3PO_3). What is the molarity of the hydrochloric acid if 750 mL of the gas, measured at STP, dissolves in 250 mL of water?

2. Why do two gases spontaneously mix when they are brought into contact?

3. The value of ΔH_{soln} for a soluble compound is, say, +26 kJ mol^{-1}, and a nearly saturated solution is prepared in an insulated container. Will the system's temperature increase or decrease as the solute dissolves? Which value for this compound would be numerically larger, its lattice energy or its hydration energy?

4. Methanol, $CH_3{-}O{-}H$, and water are miscible in all proportions. What does this mean? Explain how the O—H unit in methanol contributes to this.

5. Show that when the mole fraction of the solvent in the solution is nearly unity, the molarity (C) and molality (m) of the solution are connected by the equation.

$$C = \rho \times m$$

where ρ is the density of the solution.

6. Hexane (C_6H_{12}) and water are immiscible. What does this mean? Explain why they are immiscible in terms of structural features of their molecules and the forces of attraction between them.

7. Why is ammonia so much more soluble in water than is nitrogen? Explain.

8. When substances form liquid solutions, what two factors are involved in determining the solubility of the solute in the solvent?

9. Which would be expected to have the larger hydration energy, Al^{3+} or Li^{+}? Why? (Both ions are about the same size.)

10. If a saturated solution of NH_4NO_3 at 70°C is cooled to 10°C, how many grams of solute will separate if the quantity of the solvent is 100 g?

11. The value of ΔH_{soln} for the formation of an ethanol–hexane solution is positive, while that of acetone–water solution is negative. Explain this in general terms that involve intermolecular forces of attraction.

12. The largest fish are found in deep sinks in lake bottoms, where the water is coolest. Use the temperature dependence of oxygen solubility in water to explain why.

13. When a solid is associated in a solution, what does this mean? What difference does it make to expected colligative properties?

14. Mountain streams often contain fewer living things than equivalent streams at sea level. Give one reason why this might be true in terms of oxygen solubilities at different pressures.

15. When octane is mixed with methanol, the vapor pressure of the octane over the solution is higher than what we would calculate using Raoult's law. Why? Explain the discrepancy in terms of intermolecular attractions.

16. Why does a bottled carbonated beverage fizz when you take the cap off?

17. Suppose a 1.0 molal solution of a solute is made using a solvent with a density of 1.15 g mL^{-1}. Will the molarity of this solution be numerically larger or smaller than 1.0? Explain.

18. What kinds of data would have to be obtained to find out if a solution of two miscible liquids is almost exactly an ideal solution?
19. Explain why a non-volatile solute dissolved in water makes the system have (a) a higher boiling point than water and (b) a lower freezing point than water.
20. What specific fact about a physical property of a solution must be true to call it a colligative property?
21. At a molecular level, explain why in osmosis there is a net migration of solvent from the side of the membrane less concentrated in solute to the side more concentrated in solute.
22. What is the van't Hoff factor? What is its expected value for all non-dissociating molecular solutes? If its measured value is slightly larger than 1.0, what does this suggest about the solute? What is suggested by a van't Hoff factor of approximately 0.5?
23. Two glucose solutions of unequal molarity are separated by an osmotic membrane. Which solution will lose water, the one with the higher or the lower molarity?
24. What is the key difference between dialyzing and osmotic membranes?
25. Why are colligative properties of solutions of ionic compounds usually more pronounced than those of solutions of molecular compounds of the same molalities?
26. Which aqueous solution has the higher osmotic pressure, 10% glucose, $C_6H_{12}O_6$, or 10% sucrose, $C_{12}H_{22}O_{11}$?
27. Which aqueous solution, if either, is likely to have the higher boiling point, 0.50 molal NaI or 0.50 molal Na_2CO_3?
28. To what type of solution does an alloy belong to? Give one example of a solution of liquid in solid.

NUMERICAL PROBLEMS

1. Calculate the freezing point of an aqueous solution of electrolyte having osmotic pressure of 2.0 atm at 300 K. K_f = 1.86 K molal^{-1}, R = 0.0821 L atm K^{-1} mol^{-1}.
2. At 25°C, the vapor pressure of pure methyl alcohol is 92.0 torr. What is the mole fraction of CH_3OH in a solution in which vapor pressure of CH_3OH is 23.0 torr at 25°C?
3. The vapor pressure of pure benzene at 25°C is 640.0 mm Hg and vapor pressure of a solution of a solute in benzene is 25°C is 632.0 mm Hg. Find the freezing point of the solution if K_f for benzene is 5.12 K molal^{-1} ($T^{o}_{f(\text{Benzene})} = 5.5°\text{C}$).
4. A solution containing 2.7 g of urea per 100 mL of the solution is isotonic with a solution of sucrose. How many grams of sucrose are present in 500 mL of the solution?
5. 2.0 g of benzoic acid, C_6H_5COOH dissolve in 25.0 g of benzene show a depression in freezing point of 1.62 K. K_f of benzene = 4.9 K molal^{-1}. What is the percentage association of the acid?
6. What is the percentage by mass of iodine needed to reduce the freezing point of benzene to 3.5°C. The freezing point and cryoscopic constant of pure benzene are 5.5°C and 5.12 K molal^{-1}, respectively.
7. What is the degree of dissociation α of a weak electrolyte in terms of van't Hoff factor i and the number of ions given by 1 mol of the electrolyte, N?
8. What is the osmotic pressure of a solution made by mixing 100 mL of 0.1 M acetone and 100 mL of 0.2 M solution at 30°C?
9. In a cold climate, water gets frozen causing damage to the radiator of cars. Ethylene glycol is used as an anti-freeze. Calculate the amount of glycol to be added to 4.0 kg of water to prevent it from freezing at −6°C. K_f of water = 1.86 K molal^{-1}.
10. 0.6 L of a solute is dissolved in 0.1 L of a solvent which develops an osmotic pressure of 1.23 atm at 27°C. What is the molecular weight of the solute?
11. The boiling point elevation of 600 mg of acetic acid in 0.1 kg of benzene is 0.1265 K. What conclusion can you draw about the molecular state of acetic acid in benzene? (K_b of benzene is 2.53 K molal^{-1}.)
12. The van't Hoff factor for a 0.1 M $Al_2(SO_4)_3$ solution in 4.20. The degree of dissociation is
13. The freezing point depression of 0.1 molal NaCl solution is 0.372 K. What conclusion can you draw about, the molecular state of NaCl in water. K_f of water = 1.86 K molal^{-1}.
14. An aqueous solution containing an ionic salt having molality equal to 0.19 freezes at –0.704°C. The van't Hoff factor of the ionic salt is (Given K_f for water = 1.86 K molal^{-1})
15. A weak electrolyte XY is 5% dissociated in water. What is the freezing point of a 0.01 molal aqueous solution of XY? The cryoscopic constant of water is 1.86 K molal^{-1}.
16. Arrange the following solutions in increasing order of
    (a) boiling points (i) 0.001 molal NaCl, (ii) 0.001 molal urea, (iii) 0.001 molal $MgCl_2$ and (iv) 0.001 molal CH_3COOH.
    (b) freezing points (i) 0.1 M glucose, (iii) 1% urea solution and (iii) 0.1 M common salt.
    (c) osmotic pressure: (i) $NaNO_3$, (ii) $BaCl_2$, (iii) $K_4[Fe(CN)_6]$, (iv) $C_6H_{12}O_6$ and (iv) CH_3COOH.
17. The vapor pressure of a solution containing 5.0 g of a non-electrolyte in 100.0 g; of water at a particular temperature is 2985 N m^{-2}. If the vapor pressure of pure water is 3000 N m^{-2}, what is the molecular weight of the solution?
18. The vapor pressure of pure liquid solvent A is 0.80 atm. When a non-volatile substance B is added to the solvent, its vapor pressure drops to 0.60 atm. What is the mole fraction of the component B in the solution?
19. The vapor pressure of pure benzene, C_6H_6 at 50°C is 268 torr. How many moles of non-volatile solute per mole of benzene is required to prepare a solution of benzene having a vapor pressure of 167 torr at 50°C?

20. The molal boiling-point constant for water is 0.513 K molal^{-1}. When 0.1 mol of sugar is dissolved in 200.0 g of water, the solution boils under a pressure of 1.0 atm at what temperature?

21. The vapor pressure at a given temperature of an ideal solution containing 0.2 mol of a non volatile solute and 0.8 mol of a solvent is 60 mm Hg. What will be the vapor pressure of the pure solvent at the same temperature?

22. 10.0 g of glucose (Π_1), 10.0 g of urea (Π_2) and 10.0 g of sucrose (Π_3) are dissolved in 250.0 mL of water at 273 K (where Π = osmotic pressure of a solution). What is the relationship between the osmotic pressures of the solutions?

23. A 5% solution of cane sugar (mol. wt. = 342 g mol^{-1}) is isotonic with a 1% solution of a substance X. What is the molecular weight of X?

24. From a measurement of the freezing-point depression of benzene, the molecular weight of acetic acid in a benzene solution was determined to be 100. What is the percentage association of acetic acid?

25. What is the ratio of freezing-point depression values of 0.01 M solutions of urea, common salt and Na_2SO_4?

26. What should be the boiling point of 1.0 molal aqueous KCl solution (assuming complete dissociation of KCl) if K_b of H_2O is 0.52 K molal^{-1}?

ADDITIONAL OBJECTIVE QUESTIONS

Single Correct Choice Type

1. A solution is obtained by mixing 300 g of 25% solution and 400 g of 40% solution by mass. What will be the mass percentage of the solute and solvent of resulting solution?

(A) 23% and 77% (B) 12.5% and 87.5%
(C) 33.6% and 66.4% (D) 50% and 50%

2. A X molal solution of a compound in benzene has mole fraction of solute equal to 0.2. The value of X is

(A) 14 (B) 3.2
(C) 1.4 (D) 2.0

3. Concentrated nitric acid used in laboratory work is 68% nitric acid by mass in aqueous solution. What should be the molarity of such a sample of the acid if the density of the solution is 1.504 g L^{-1}.

(A) 1.623 M (B) 16.23 M
(C) 162.3 M (D) 0.1623 M

4. One liter of sea water weighs 1030.g and contains about 6×10^3 g dissolved O_2. What will be the concentration of dissolved oxygen in ppm?

(A) 68 ppm (B) 5.8 ppm
(C) 580 ppm (D) 0.58 ppm

5. An antifreeze solution is prepared from 222.6 g of ethylene glycol ($C_2H_6O_2$) and 200 g of water. What will be the molality and molarity of the solution respectively? (Given that the density of the solution is 1,072 g mL^{-1}.)

(A) 17.95, 91.1 (B) 17.95, 9.11
(C) 1.795, 9.11 (D) 1.795, 91.1

6. What will be the (i) molality (ii) molarity and (iii) mole fraction of KI, respectively, if the density of 20% (mass/mass) aqueous KI is 1.202 g mL^{-1}?

(A) 1.5, 1.45 and 0.0263 (B) 15, 14.5 and 0.0263
(C) 1.5, 14,5 and 0.0263 (D) 1.5, 1.45 and 0.263

7. Vapor pressure of CCl_4 at 25°C is 143 mm Hg. If 0.5 g of a non-volatile solute (mol. wt. 65) is dissolved in 100 mL CCl_4, find the vapor pressure of the solution. (Given that density of CCl_4 = 1.58 g cm^{-3}.)

(A) 141.93 mm Hg (B) 94.39 mm Hg
(C) 199.34 mm Hg (D) 143.99 mm Hg

8. Two liquids A and B arc mixed at temperature T in a certain ratio to form an ideal solution, it was found that the partial vapor pressure of A, that is, p_A is equal to p_B the vapor pressure of B for the liquid mixture. What is the total vapor pressure of the liquid mixture in terms of p_A^o and p_B^o?

(A) $\dfrac{p_A^o p_B^o}{p_A^o + p_B^o}$ (B) $\dfrac{2p_A^o p_B^o}{p_A^o + p_B^o}$

(C) $\dfrac{p_A^o}{p_A^o + p_B^o}$ (D) $\dfrac{2p_B^o}{p_A^o + p_B^o}$

9. The partial pressure of ethane over a solution containing 6.56×10^{-3} g of ethane is 1 bar. If the solution contains 5.00×10^{-2} g of ethane, then what shall be the partial pressure of the gas?

(A) 76.2 bar (B) 762 bar
(C) 0.762 bar (D) 7.62 bar

10. Henry's law constant for the molality of methane in benzene at 298 K is 4.27×10^5 mm Hg. Determine the solubility of methane in benzene at 298 K under 760 mm Hg.

(A) 178×10^{-3} (B) 178×10^{-5}
(C) 356×10^{-5} (D) 356×10^{-3}

11. The relative lowering of vapor pressure is equal to the mole fraction of the solute. This law is called

(A) Henry's law (B) Raoult's law
(C) Ostwald law (D) Arrhenius law

12. An aqueous solution of methanol has vapor pressure

(A) equal to that of water. (B) equal to that of methanol.
(C) more than that of water. (D) less than that of water.

13. Which of the following statements is correct, if the intermolecular forces in liquids A, B and C are in the order $A < B < C$?

(A) B evaporates more readily than A
(B) B evaporates less readily than C
(C) A and B evaporate at the same rate
(D) A evaporates more readily than C

14. An ideal solution was obtained by mixing methanol and ethanol. If the partial vapor pressure of methanol and ethanol are 2.619 kPa and 4.556 kPa, respectively, the composition of vapor (in terms of mole fraction) will be

(A) 0.634 MeOH, 0.365 EtOH
(B) 0.365 MeOH, 0.635 EtOH
(C) 0.574 MeOH, 0.326 EtOH
(D) 0.173 MeOH, 0.827 EtOH

15. At 35°C the vapor pressure of CS_2 is 512 mm Hg, and of acetone, CH_3COCH_3, is 344 mm Hg. A solution of CS_2 and acetone in which the mole fraction of CS_2 is 0.25 has a total vapor pressure of 600 mm Hg. Which of the following statements about solution of acetone–CS_2 is true?
(A) A mixture of 100 mL of acetone and 100 mL of CS_2 has a total volume of 200 mL.
(B) When acetone and CS_2 are mixed at 25°C, heat must be absorbed in order to produce a solution at 35°C.
(C) When acetone and CS_2 are mixed at 35°C, heat is released.
(D) Raoult's law is obeyed by both CS_2 and acetone for the solution in which the mole fraction of CS_2 is 0.25.

16. What is the composition of the vapor which is in equilibrium at 30°C with a benzene–toluene solution with a mole fraction of benzene of 0.400? ($p^{\circ}_{B} = 119$ torr and $p^{\circ}_{T} = 37.0$ torr)
(A) 1.237
(B) 2.237
(C) 3.237
(D) 0.237

17. At a given temperature, total vapor pressure in torr of a mixture of volatile components A and B is given by $p_{\text{total}} = 120 - 75x_{B,}$ hence, vapor pressure of pure A and B, respectively, (in torr) are
(A) 120, 75
(B) 120, 195
(C) 20, 45
(D) 75, 45

18. Liquids A and B form an ideal solution and the former has stronger intermolecular forces. If x_A and y_A are the mole fractions of A in the solution and vapor phase in equilibrium, then
(A) $y_A/x_A = 1$
(B) $y_A/x_A > 1$
(C) $y_A/x_A < 1$
(D) $y_A + x_A = 1$

19. Benzene and toluene form ideal solution over the entire range of composition. The vapor pressure of pure benzene and naphthalene at 300 K are 50.71 mm Hg and 32.06 mm Hg respectively. What will be the mole fraction of benzene in vapor phase if 80 g of benzene is mixed with 100 g of naphthalene?
(A) 0.0675
(B) 0.675
(C) 0.35
(D) 0.5

20. 100 g of liquid A (molar mass 140 g mol^{-1}) was dissolved in 1000 g of liquid B (molar mass 180 g mol^{-1}). The vapor pressure of pure liquid B was found to be 500 torr. What will be the vapor pressure of pure liquid A and its vapor pressure in the solution, respectively, if the total vapor pressure of the solution is 475 torr?
(A) 28.7 torr and 32 torr
(B) 280.7 torr and 32 torr
(C) 28.7 torr and 3.2 torr
(D) 280.7 torr and 3.2 torr

21. Liquids A and B form an ideal solution, then which of the following is true?
(A) The enthalpy of mixing is zero.
(B) The entropy of mixing is zero.
(C) The free energy of mixing is zero.
(D) The ΔV_{mix} of mixing is not zero.

22. 100 mL of liquid A was mixed with 25 mL of liquid B to give a non-ideal solution of A–B mixture. The volume of this mixture would be
(A) 75 mL.
(B) either less or more than 125 mL.
(C) close to 125 mL but not exceeding 125 mL.
(D) just more than 125 mL.

23. If p°_{A} is the vapor pressure of a pure liquid A and the mole fraction of A in the mixture of two liquids A and B is x, the partial vapor pressure of A is
(A) $(1 - x)\, p^{\circ}_{A}$
(B) $x p^{\circ}_{A}$
(C) $(x/1 - x)\, p^{\circ}_{A}$
(D) $[(1 - x)/x]\, p^{\circ}_{A}$

24. In a mixture of A and B if the mole fraction of the component A in vapor phase is x_1 and mole fraction of component A in liquid mixture is x_2 (p°_{A} = vapor pressure of pure A; p°_{B} = vapor pressure of pure B), then total vapor pressure of the liquid mixture is:
(A) $\dfrac{p^{\circ}_{A}x_2}{x_1}$
(B) $\dfrac{p^{\circ}_{A}x_1}{x_2}$
(C) $\dfrac{p^{\circ}_{B}x_1}{x_2}$
(D) $\dfrac{p^{\circ}_{B}x_2}{x_1}$

25. Heptane and octane form an ideal solution. At 373 K, the vapor pressures of the two liquid components are 105.2 kPa and 46.8 kPa, respectively. What will be the vapor pressure of a mixture of 26.0 g of heptane and 35 g of octane?
(A) 7.308 kPa
(B) 73.08 kPa
(C) 730.8 kPa
(D) 7308 kPa

26. At 40°C, the vapor pressure in torr of methanol and ethanol solution is $p = 119x + 135$, where x is the mole fraction of methanol. Hence,
(A) vapor pressure of pure methanol is 119 torr.
(B) vapor pressure of pure ethanol is 135 torr.
(C) vapor pressure of equimolar mixture of each is 127 mm Hg.
(D) mixture is completely immiscible.

27. A solution that obeys Raoult's law is
(A) non-ideal.
(B) colloid.
(C) ideal.
(D) saturated.

28. In a mixture, A and B components show negative deviation as
(A) ΔV_{mix} is positive.
(B) ΔH_{mix} = negative.
(C) A–B interaction is weaker than A–A and B–B interaction.
(D) None of the above reason is correct.

29. The vapor pressure of a solvent decreased by 10 mm Hg when a non-volatile solute was added to the solvent. The mole fraction of the solute in solution is 0.2. What would be mole fraction of the solvent if decrease in vapor pressure is 20 mm Hg?
(A) 0.8
(B) 0.6
(C) 0.4
(D) 0.2

30. The vapor pressure of ethyl alcohol at 25°C is 59.2 torr. The vapor pressure of a very dilute solution of urea in

ethyl alcohol is 51.3 torr. What is the molality of the solution?
(A) 29 molal (B) 2.9 molal
(C) 0.29 molal (D) 1.5 molal

31. Which of the following liquid pairs shows a positive deviation from Raoult's law?
(A) Water–nitric acid
(B) Benzene–methanol
(C) Water–hydrochloric acid
(D) Acetone-chloroform

32. All form ideal solution except
(A) C_2H_5Br and C_2H_5I (B) C_6H_5Cl and C_6H_5Br
(C) C_6H_6 and $C_6H_5CH_3$ (D) C_2H_5I end C_2H_5OH

33. The vapor pressure of a pure liquid A is 40 mm Hg at 310 K. The vapor pressure of this liquid in a solution with liquid B is 32 mm Hg. Mole fraction of A in the solution, if it obeys Raoult's law, is
(A) 0.8 (B) 0.5
(C) 0.2 (D) 0.4

34. Mole fraction of the component A in vapor phase is x_1 and mole fraction of component A in liquid mixture is x_2 (p_A^o = vapor pressure of pure A), then total vapor pressure of the liquid mixture is

(A) $\dfrac{p_A^o x_2}{x_1}$ (B) $\dfrac{p_A^o x_1}{x_2}$

(C) $\dfrac{p_B^o x_1}{x_2}$ (D) $\dfrac{p_B^o x_2}{x_1}$

35. Negative deviations from Raoult's law are exhibited by binary liquid mixtures
(A) in which the molecules tend to attract each other and hence their escape into the vapor phase is retarded.
(B) in which the molecules tend to repel each other and hence their escape into the vapor phase is retarded.
(C) in which the molecules tend to attract each other end hence their escape into the vapor phase is speeded up.
(D) in which the molecules tend to repel each other and hence their escape into the vapor phase is speeded up.

36. A non-ideal solution was prepared by mixing 30 mL chloroform and 50 mL acetone. The volume of mixture will be
(A) > 80 mL. (B) < 80 mL.
(C) = 80 mL. (D) none of these.

37. A solution of pair of volatile liquids A and B will show positive deviation from Raoult's law if it fulfills the following conditions:
(A) $p_A > p_A^o x_A$ and $p_B > p_B^o x_B$
(B) The intermolecular forces of A – A, B – B >A – B
(C) $\Delta H_{mix} > 0$ and $\Delta V_{mix} > 0$
(D) All of these

38. Which of the following is not a colligative property?
(A) Osmotic pressure
(B) Elevation in boiling point.
(C) Vapor pressure.
(D) Depression in freezing point.

39. The colligative properties of a solution depend on
(A) nature of solute particles present in it.
(B) nature of solvent used.
(C) number of solute particles present in it
(D) number of moles of solvent only.

40. A dry air is passed through the solution, containing the 10 g of solute and 90 g of water and then it pass through pure water. There is the depression in weight of solution by 2.5 g and of pure solvent by 0.05 g. Calculate the molecular weight of solute.
(A) 50 (B) 180
(C) 100 (D) 25

41. The vapor pressure of a solvent decreased by 10 mm Hg when a non-volatile solute was added to the solvent. The mole fraction of solute in solution is 0.2, what would be mole fraction of the solvent if decrease in vapor pressure is 20 mm Hg?
(A) 0.8 (B) 0.6
(C) 0.4 (D) 0.2

42. The vapor pressure of water is 12.3 kPa at 300 K. What will be the vapor pressure of 1 molal solution if a non-volatile solute is added to it?
(A) 24.16 kPa (B) 1.208 kPa
(C) 2.416 kPa (D) 12.08 kPa

43. What will be the mass of a non-volatile solute (molar mass 40 mol^{-1} which should be dissolved in 114 g octane to reduce its vapor pressure to 80%?
(A) 8 g (B) 4 g
(C) 2 g (D) 16 g

44. An aqueous solution freezes at –2.55°C. What is its boiling point? (Given that K_b of H_2O = 0.52 K molal^{-1} and K_f of H_2O = 1.86 K molal^{-1}.)
(A) 107.0°C (B) 100.6°C
(C) 100.1°C (D) 100.7°C

45. Vapor pressure of water at 293 K is 17.535 mm Hg. What will be the vapor pressure of water at 293 K when 25 g of glucose is dissolved in 450 g of water?
(A) 17.44 mm Hg (B) 174.4 mm Hg
(C) 34.88 mm Hg (D) 8.72 mm Hg

46. The boiling point of an aqueous solution of a non-volatile solute is 100.15°C. What is the freezing point of an aqueous solution obtained by diluting the above solution with an equal volume of water? The values of K_b and K_f for water are 0.412°C molal^{-1} and 1.86°C molal^{-1}, respectively.
(A) –0.544°C (B) –0.512°C
(C) –0.272°C (D) –1.86°C′

47. The boiling point elevation constant for toluene is 3.32 K kg mol^{-1}, the normal boiling point of toluene is 110.7°C. The enthalpy of vaporization of toluene would by nearly
(A) 17.0 kJ mol^{-1} (B) 34.0 kJ mol^{-1}
(C) 51.0 kJ mol^{-1} (D) 68.0 kJ mol^{-1}

48. The molal elevation constant is the ratio of the elevation in boiling point to
(A) molarity. (B) molality.
(C) mole fraction of solute. (D) mole fraction of solvent.

49. 0.15 g of a substance dissolved in 15 g of a solvent is boiled at a temperature higher by 0.216°C than that of the pure solvent. Find out the molecular weight of the substance. (K_f for solvent is 2.16 K kg mol^{-1}).
(A) 1.01 g mol^{-1} (B) 10.1 g mol^{-1}
(C) 100 g mol^{-1} (D) 1000 g mol^{-1}

50. Y g of non-volatile organic substance of molecular mass M is dissolved in 250 g benzene. Molal elevation constant of benzene is K_b. Elevation in its boiling point is given by
(A) $\dfrac{M}{K_bY}$ (B) $\dfrac{4K_bY}{M}$
(C) $\dfrac{K_bY}{4M}$ (D) $\dfrac{K_bY}{M}$

51. The molal boiling point constant of water is 0.573°C kg mol^{-1}. When 0.1 mol of glucose is dissolved in 1000 g of water, the solution boils under atmospheric pressure at
(A) 100.513°C (B) 100.0573°C
(C) 100.256°C (D) 101.025°C

52. It is more a convenient to obtain the molecular weight of an unknown solute by measuring the freezing point depression than by measuring the boiling point elevation because
(A) freezing point depression is a colligative property whereas boiling point elevation is not.
(B) freezing point depressions are larger than boiling point elevations for the same solution.
(C) freezing point depressions are smaller than boiling point elevations for the same solution.
(D) freezing point depression depends more on the amount of the solute than boiling point elevation.

53. The freezing point of aqueous solution contains 5% by mass urea, 1.0% by mass KCl and 10% by mass of glucose is (Given that K_f of H_2O = 1.86 K molal^{-1}.)
(A) 290.2 K (B) 285.5 K
(C) 269.93 K (D) 250 K

54. In 100 g of naphthalene, 2.423 g of S was dissolved. Melting point of naphthalene = 80.1°C, ΔT_f = 661°C and latent heat of fusion, L_{fus} = 35.7 cal g^{-1} of naphthalene. Then the molecular formula of sulphur added is
(A) S_2 (B) S_4
(C) S_6 (D) S_8

55. Osmotic pressure of blood is 7.65 atm at 310 K. An aqueous solution of glucose that will be isotonic with blood is ________ %(w/V).
(A) 5.41% (B) 3.54%
(C) 4.53% (D) 53.4%

56. A 5% solution (by mass) of cane sugar in water has freezing point of 271 K. What will be the freezing point of 5% glucose in water if freezing point of pure water is 273.15 K?
(A) 273.15 K (B) 279.07 K
(C) 260.07 K (D) 203.07 K

57. Two elements A and B form compounds having formulas AB_2 and AB_4. When dissolved in 20 g of benzene (C_6H_6), 1 g of AB_2 lowers the freezing point by 2.3 K whereas 1.0 g of AB_4 lowers it by 1.3 K. The molar depression constant for benzene is 5.1 K kg mol^{-1}. What will be the atomic masses of A and B, respectively?
(A) 26 u, 42.5 u (B) 52 u, 42.5 u
(C) 26 u, 85 u (D) 52 u, 85 u

58. The molal freezing point constant for water is 1.86 K. molality^{-1}. If 34.2 g of cane sugar ($C_{12}H_{22}O_{11}$) are dissolved in 1000 g of water, the solution will freeze at
(A) –1.86°C (B) 1.86°C
(C) –3.92°C (D) 3.42°C

59. Which one of the following pairs of solution can we expect to be isotonic at the same temperature?
(A) 0.1 M urea mid 0.1 M NaCl
(B) 0.1 M urea and 0.2 M $MgCl_2$
(C) 0.1 M NaCl and 0.1 M Na_2SO_4
(D) 0.1 M $Ca(NO_3)_2$ and 0.1 M Na_2SO_4

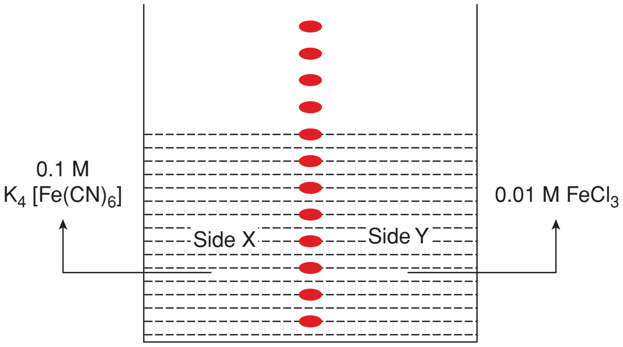
60. What is the percent by mass of iodine needed to reduce the freezing point of benzene to 3.5°C? The freezing point and cryoscopic constant of pure benzene are 5.5°C and 5.12 K molal^{-1}, respectively, are
(A) 20% (B) 90.1%
(C) 30% (D) 9.01%

61. The amount of ice that will separate on cooling a solution containing 50 g of ethylene glycol in 200 g water to –9.3°C is: [K_f = 1.86 K molal^{-1}]
(A) 38.71 g (B) 38.71 mg
(C) 42 g (D) 42 mg

62. At 300 K, 36 g of glucose present in a liter of its solution has osmotic pressure of 4.98 bar. If the osmotic pressure of the solution is 1.52 bar at the same temperature, what would be its concentration?
(A) 0.061 M (B) 0.61 M
(C) 0.0061 M (D) 6.1 M

63. Nitrobenzene freezes at 278.98°C, 0.25 molal solution of a solute in nitrobenzene causes freezing point depression of 2°C. K_f for nitrobenzene is
(A) 2 K molal^{-1} (B) 4 K molal^{-1}
(C) 8 K molal^{-1} (D) 12 K molal^{-1}

64. $FeCl_3$ on reaction with $[K_4(Fe(CN)_6]$ in aqueous solution gives blue color. These are separated by a semipermeable membrane AB. Due to osmosis there is
(A) blue color formation in side X.
(B) blue color formation in side Y.
(C) blue color formation in both sides
(D) no blue color formation.



65. Consider following cases:
I: 2 M CH_3COOH solution in benzene at 27°C where there is formation to the extent of 100%.
II: 0.5 M KCl aqueous solution at 27°C, which ionizes 100%.
Which is/are true statement(s)?

(A) both are isotonic.
(B) I is hypertonic.
(C) II is hypertonic.
(D) none is correct.

66. Boiling point of pure H_2O is 373.15 K. If 32.5 g of KCN is dissolved in 100 mL of H_2O, what will the the boiling point of solution? (Given K_b for $H_2O = 0.52$ K kg mol^{-1} and molar mass of KCN = 65 g mol^{-1}.)
(A) 105.20°C
(B) 100.52°C
(C) 373.67 K
(D) 273.67 K

67. A 5% solution of cane sugar (mol. wt. = 342 g mol^{-1}) is isotonic with 1% solution of substance X. The molecular weight of X is
(A) 17.12 g mol^{-1}
(B) 68.4 g mol^{-1}
(C) 34.2 g mol^{-1}
(D) 136.2 g mol^{-1}

68. Which of the following aqueous solutions will have the lowest freezing point?
(A) 0.10 M KCl
(B) 0.10 M $Al_2(SO_4)_3$
(C) 0.10 M $C_6H_{12}O_6$
(D) 0.10 M $C_{12}H_{22}O_{11}$

69. Which of the following solution (in H_2O) has highest boiling point elevation?
(A) 0.2 M urea
(B) 0.1 M $K_4[Fe(CN)_6]$
(C) 0.2 M K_2SO_4
(D) 0.3 M Glucose

70. Arrange the following compounds in order of decreasing the depression in freezing point of water of water for the same molarity:
(I) Acetic acid
(II) Trichloroacetic acid
(III) Trifluoroacetic acid
(A) I > II > III
(B) II > III > I
(C) III > I > II
(D) III > II > I

71. The osmotic pressure of a 5% aqueous solution of cane sugar at 150°C is (Mol. wt. of cane sugar = 342 g mol^{-1}.)
(A) 4 atm
(B) 3.4 atm
(C) 5.07 atm
(D) 2.45 atm

72. If 32 g of an unknown molecule (assumed to be unionized in solution) dissolved in 200 g of H_2O, then elevation in boiling point is found to be 1.04°C. Find out the molar mass of the unknown molecule (given K_b for H_2O = 0.52 K kg mol^{-1}.)
(A) 160 g mol^{-1}
(B) 80 g mol^{-1}
(C) 40 g mol^{-1}
(D) 320 g mol^{-1}

73. The ratio of the value of any colligative property for KCl solution to that for sugar is nearly _____ times (for the same molality and solvent).
(A) 1
(B) 0.5
(C) 2
(D) 2.5

74. The freezing point of a solution of acetic acid (mole fraction is 0.02) in benzene is 277.4 K. Acetic acid exists partly as a dimer $2A \rightleftharpoons A_2$. Determine the equilibrium constant for dimerization. Freezing point of benzene is 278.4 K and K_f for benzene is 5 K molal^{-1}.
(A) 3.19 kg mol^{-1}
(B) 31.9 kg mol^{-1}
(C) 1.6 kg mol^{-1}
(D) 16.0 kg mol^{-1}

75. 0.01 M solution each of urea, common salt and Na_2SO_4 are taken. The ratio of depression of freezing point is
(A) 1:1:1
(B) 1:2:1
(C) 1:2:3
(D) 2:2:3

76. If the solution of mercuric cyanide of strength 3 g L^{-1} has an osmotic pressure 0.3092×10^5 Nm^{-2} at 298 K, what is the apparent molecular weight and degree of dissociation of $Hg(CN)_2$, respectively? (Given atomic masses as Hg = 200.61 u, C = 12 u, N = 14 u.)
(A) 240.2, 2.45%
(B) 480.4, 2.45%
(C) 480.4, 24.5%
(D) 240.2, 24.5%

77. When mercuric iodide is added to the aqueous solution of potassium iodide, the:
(A) freezing point is raised.
(B) freezing point is lowered.
(C) freezing point docs not change.
(D) boiling point does not change.

78. The freezing point of 1 molal NaCl solution assuming NaCl to be 100% dissociated in water is (K_f for H_2O = 1.86°C molal^{-1}.)
(A) –1.86°C
(B) –3.72°C
(C) +1.86°C
(D) –3.72°C.

79. When 1000 g of 1 molal sucrose solution in water is cooled to –3.534°C, the mass of ice separated out at this temperature will be (K_f for H_2O = 1.86 °C molal^{-1}.)
(A) 353.19 g
(B) 252.9 g
(C) 52.98 g
(D) 152.98 g

80. How much the amount of $CaCl_2$ (i = 2.47) dissolved in 2.5 L of water such that its osmotic pressure is 0.75 atm at 27°C?
(A) 0.3 mol
(B) 0.03 mol
(C) 3 mol
(D) 0.003 mol

81. What will be the osmotic pressure of a solution prepared by dissolving 25 mg of K_2SO_4 in 2 L of water at 25°C, assuming that it is completely dissociated?
(A) 5.27×10^{-3} atm
(B) 52.7×10^{-3} atm
(C) 26.3×10^{-3} atm
(D) 2.03×10^{-3} atm

82. The values of observed and calculated molecular weights of silver nitrate are 92.64 g mol^{-1} and 170 g mol^{-1}, respectively. The degrees of dissociation of silver nitrate is
(A) 60%
(B) 83.5%
(C) 46.7%
(D) 60.23%

83. Which of the following solutions will have the highest boiling point?
(A) 1% glucose
(B) 1% sucrose
(C) 1% NaCl
(D) 1% $CaCl_2$

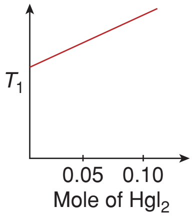
84. Acetic acid exists in benzene solution in the dimeric form. In an actual experiment, the van't Hoff factor was found to the 0.52. Then the degree of dissociation of acetic acid is
(A) 0.48
(B) 0.88
(C) 0.96
(D) 0.52

85. The average osmotic of human blood is 7.8 bar at 37°C. What is the concentration of an aqueous NaCl solution that could be used in the blood stream?
(A) 0.15 mol L^{-1}
(B) 0.30 mol L^{-1}
(C) 0.60 mol L^{-1}
(D) 0.45 mol L^{-1}

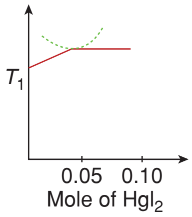
86. Three particles of a solute, A, associate in benzene to form species A_3. Determine the freezing point of 0.25 molal solution. The degree of association of solute A is found to be 0.80. The freezing point of benzene and its cryoscopic constant are 5.5°C and 5.12 K molal^{-1}, respectively.
(A) 49°C
(B) 4.9°C
(C) 25°C
(D) 2.5°C

87. Increasing amount of solid HgI_2 is added to 1 L of an aqueous solution containing 0.1 mol KI. Which of the following graphs represents the variation of freezing point of the resulting with the amount of HgI_2 added?

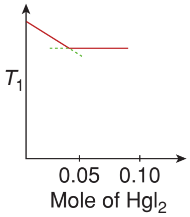
(A)



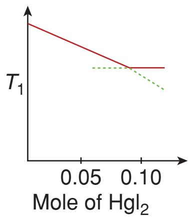
(B)



(C)



(D)



88. Equimolal solutions KCl and compound X in water show depression in freezing point in the ratio of 4:1. Assuming KCl to be completely ionized, the compound X in solution must

(A) dissociate to the extent of 50%.
(B) hydrolyze to the extent of 80%.
(C) dimerize to the extent of 50%.
(D) trimerize to the extent of 75%.

89. Among the following, the solution which shows the lowest osmotic pressure is:

(A) 0.10 M NaCl
(B) 0.05 M $CaCl_2$
(C) 0.04 M $K_3[Fe(CN)_6]$
(D) 0.03 M $FeCl_3$

90. Calculate the boiling point of a one molar aqueous solution (density = 1.04 g mL^{-1}) of potassium chloride, K_b for water = 0.52 kg mol^{-1}. (Atomic masses of K = 39 u, Cl = 35.5 u)

(A) 107.28°C
(B) 103.68°C
(C) 101.078°C
(D) None of these

91. Maximum freezing point will be for 1 molal solution of, assuming equal ionization in each case,

(A) $[Fe(H_2O)_6]Cl_3$
(B) $[Fe(H_2O)_5Cl]Cl_2{\cdot}H_2O$
(C) $Fe(H_2O)_4Cl_2]Cl{\cdot}2H_2O$
(D) $[Fe(H_2O)_3Cl_3]{\cdot}3H_2O$

Multiple Correct Choice Type

1. When a solute is added to a pure solvent, the

(A) vapor pressure of the solution becomes lower than that of the pure solvent.
(B) rate of evaporation of the pure solvent is reduced.
(C) solute does not affect the rate of condensation.
(D) rate of evaporation of the solution is equal to the rate of condensation of the solution at a lower vapor pressure than that in the case of the pure solvent.

2. An ideal solution is formed, when

(A) its components have the same intermolecular attractions in solution as in pure components.
(B) $\Delta H_{mix} = 0$.
(C) $\Delta V_{mix} > 0$.
(D) $\Delta S_{mix} > 0$.

3. Which is/are correct statement(s)?

(A) When mixture is less volatile, there is positive deviation from Raoult's law.
(B) When mixture is more volatile, there is negative deviation from Raoult's law.
(C) When mixture is less volatile, there is negative deviation from Raoult's law.
(D) When mixture is more volatile, there is positive deviation from Raoult's law.

4. Identify the correct statements.

(A) The solution formed by mixing equal volumes of 0.1 M urea and 0.1 M glucose will have the same osmotic pressure.
(B) 0.1 M $K_4[Fe(CN)_6]$ and 0.1 M $Al_2(SO_4)_3$ are isotonic solutions.
(C) For association of a solute in a solution, $i > 1$.
(D) The ratio of van't Hoff factors for 0.2 M glucose and 0.1 M sucrose is 2:1.

5. In the depression of freezing point experiment, it is found that the

(A) vapor pressure of the solution is less than that of pure solvent.
(B) vapor pressure of the solution is more than that of pure solvent.
(C) only ionic molecules solidify at the freezing point.
(D) only solvent molecules solidify at the freezing point.

6. 1 mol benzene ($p^{o}_{benzene} = 42$ mm Hg) and 2 mol toluene ($p^{o}_{toluene} = 36$ mm Hg) will have:

(A) total vapor pressure 38 mm Hg.
(B) mole fraction of vapors of benzene above liquid mixture is 7/19.
(C) positive deviation from Raoult's law.
(D) negative deviation from Raoult's law.

7. Which of the following are correct about Henry's constant, K_H?

(A) Greater the value of K_H, lower is the solubility of the gas at the same pressure and temperature.
(B) K_H decreases with increase of temperature.
(C) The unit of K_H is bar.
(D) All noble gases have the same value of K_H at the same temperature.

8. The azeotropic solutions of two miscible liquids

(A) can be separated by simple distillation.
(B) may show positive or negative deviation from Raoult's law.
(C) are supersaturated solutions.
(D) behave like a single component and boil at a constant temperature.

9. Solution showing positive deviation from Raoult's law include

(A) Acetone + Carbon disulphide
(B) Acetone + Ethyl alcohol
(C) Acetone + Benzene
(D) Acetone + Aniline

10. Which of the following is/are incorrect? (M is assumed to be equal to m.)
(A) 1 M NaCl solution has higher freezing point than 1 M glucose solution.
(B) 1 M glucose solution has same boiling point as J M sucrose solution.
(C) Molecular weight of benzoic acid in benzene will be doubled than expected.
(D) van't Hoff factor $i > 1$ if solute undergoes association.

11. Which of the following aqueous solution are isotonic (R = 0.082 atm K^{-1} mol^{-1})?
(A) 0.01 M glucose
(B) 0.01 M $NaNO_3$
(C) 500 mL solution containing 0.3 g urea
(D) 0.04 N HCl

12. Which of the following statements are correct about the solubility of gases in liquids?
(A) Mole fraction of the gas in the solution is directly proportional to the partial pressure of the gas above the solution.
(B) Volume of the gas dissolved measured at the pressure used is independent of the pressure of the gas.
(C) Solubility of gas is always an exothermic process.
(D) Gibbs energy change of dissolution of a gas may be positive or negative.

13. Which relations are correct for an aqueous dilute solution of K_3PO_4 if its degree of dissociation is α?

(A) $\dfrac{\Delta p}{p^{\circ}} = \dfrac{m \times 18 \times (1+3\alpha)}{1000}$

(B) $\dfrac{\Delta p}{p^{\circ}} = \dfrac{\Pi_{\text{obs}} \times 18 \times (1+3\alpha)}{ST \times 1000}$

(C) $\dfrac{\Delta p}{p^{\circ}} = \dfrac{\Delta T_{\text{f obs}} \times 18}{K_f \times 1000}$ $\dfrac{\Delta p}{p^{\circ}} = \dfrac{\Delta T_{\text{f obs}} \times 18}{K_f \times 1000}$

(D) Mol. wt. of K_3PO_4 = Mol. wt.$_{\text{obs}} \times (1 + 3\alpha)$

14. Two liters of 1 molar solution of a complex salt $CrCl_3 \cdot 6H_2O$ (mol. wt. = 266.5 g mol^{-1}) shows an osmotic pressure of 98.52 atm. The solution is now treated with 1 L of 6 M $AgNO_3$. Which of the following are correct?
(A) Weight of AgCl precipitated is 861 g.
(B) The clear solution will show an osmotic pressure = 98.52 atm.
(C) The clear solution will show an osmotic pressure = 65.68 atm.
(D) 2 mol of $[Cr(H_2O)_6](NO_3)_3$ will be present in solution.

15. Two miscible liquids A and B having vapor pressure in pure state p°_A and p°_B are mixed in mole fraction x_A and x_B to get a mixture having total vapor pressure of mixture p_{total}. Which of the following relations are correct?

(A) $x_A = \dfrac{p_{\text{total}} - p^{\circ}_B}{p^{\circ}_A - p^{\circ}_B}$

(B) $\dfrac{x_{A(l)}}{x'_{A(v)}} = \dfrac{p_{\text{total}}}{p^{\circ}_A}$

(C) $\dfrac{x_{A(l)}}{x'_{A(v)}} = \dfrac{p_{\text{total}}}{p^{\circ}_B}$

(D) All of these

16. 1 mol benzene ($p^{\circ}_{\text{benzene}} = 42$ mm Hg) and 2 mol toluene ($p^{\circ}_{\text{toluene}} = 36$ mm Hg) will have
(A) total vapor pressure 38 mm Hg.
(B) mole fraction of vapors of benzene above liquid mixture of 7/19.
(C) positive deviation from Raoult's law.
(D) negative deviation from Raoult's law.

17. Dry air is passed though a set of inter connected air tight vessel containing a solution of non-volatile solute and then through another set of vessels containing pure solvent. If the solution and the solvent suffer losses of mass to be w_1 and w_2, respectively, then
(A) w_1 0 p_s
(B) w_2 0 p°
(C) w_2 0 $p^{\circ} - p_s$
(D) $(w_1 + w_2)$ 0 p°

18. Which pair(s) of liquids on mixing are expected to show no net volume change and no heat effect?
(A) Acetone and ethanol
(B) Chlorobenzene and bromobenzene
(C) Chloroform and benzene
(D) *n*-Butyl chloride and *n*-butyl bromide

19. Which of the following statements is correct?
(A) The freezing point of water is depressed by the addition of glucose.
(B) The degree of dissociation of a weak electrolyte decreases as its concentration decreases.
(C) Energy is released when a substance dissolves in water provided that the hydration energy of the substance is more than its lattice energy.
(D) If two liquids have form an ideal solution are mixed, the change in entropy is positive.

20. What does not change on changing temperature?
(A) Mole fraction
(B) Normality
(C) Molality
(D) None of these

Assertion–Reasoning Type

Choose the correct option from the following:
(A) Statement 1 and Statement 2 are True; Statement 2 is the correct explanation for Statement 1.
(B) Statement 1 and Statement 2 are True; Statement 2 is NOT the correct explanation for Statement 1.
(C) Statement 1 is True but Statement 2 is False.
(D) Statement 1 is False; Statement 2 is True.

1. **Statement 1:** Gases always tend to be less soluble in liquids as the temperature is raised.

Statement 2: Vapor pressure of liquids increase with increase in temperature.

2. **Statement 1:** The vapor pressure of a liquid is the equilibrium constant of liquid–vapor equilibrium at the given temperature.

Statement 2: The ratio of the lowering of vapor pressure of a solvent upon dissolution of a non-volatile solute to the vapor pressure of pure solvent increases with temperature.

3. **Statement 1:** Ebullioscopy or cryoscopy cannot be used for the determination of molecular weight of polymers.

   Statement 2: High molecular weight solute leads to very low value of ΔT_b or ΔT_f.

4. **Statement 1:** Reverse osmosis is used to purify saline water.

   Statement 2: Solvent molecules pass from concentrated to dilute solution through semipermeable membrane if high pressure is applied on solution.

5. **Statement 1:** If a solution is heated such that keeping rest of all things unchanged, volume is changed, then it also brings changes to colligative properties related with it.

   Statement 2: The molarity of solution changes on changing the volume of solution for the same amount of solute.

6. **Statement 1:** The boiling point of 0.1 M urea solution is less than that of 0.1 M KCl solution.

   Statement 2: Elevation of boiling point is directly proportional to the number of species present in the solution.

7. **Statement 1:** Vapor above a mixture of two liquids that does not obey Raoult's law is always richer in more volatile liquid.

   Statement 2: Azeotropic mixture gives off a vapor of same composition as that of liquid.

8. **Statement 1:** Out of various colligative properties, osmotic pressure is used for determination of molecular masses of polymers.

   Statement 2: Polymer solutions do not possess constant boiling point or freezing point.

9. **Statement 1:** Azeotropic mixtures are formed only by non-ideal solutions.

   Statement 2: Boiling point of an azeotrope is either higher than both the components or lower than both the components.

10. **Statement 1:** Only temperature can change the vapor pressure of a pure liquid.

    Statement 2: Equilibrium constant does not change unless temperature is changed.

Linked–Comprehension Type

Read the paragraphs and answer the questions that follow.

Paragraph I

On dissolving 68.4 g of sucrose in 1 kg of water, a solution of sucrose with molar mass 342 g mol^{-1} is formed. K_f for water is 1.86 K kg mol^{-1} and vapor pressure of water at 298 K is 0.024 atm.

1. The vapor pressure of the solution at 298 K will be
   (A) 0.230 atm. (B) 0.233 atm.
   (C) 0.236 atm. (D) 0.0239 atm.

2. The osmotic pressure of the solution at 298 K will be
   (A) 4.29 atm. (B) 4.49 atm.
   (C) 4.69 atm. (D) 4.89 atm.

3. The freezing point of the solution will be
   (A) –0.684°C. (B) –0.342°C.
   (C) –0.372°C. (D) –0.186°C.

4. The mass of sodium chloride that should be dissolved in the same amount of water to get the same freezing point will be
   (A) 136.8 g. (B) 32.2 g.
   (C) 5.85 g. (D) 11.60 g.

5. If on dissolving the above amount of NaCl in 1 kg of water, the freezing point is found to be –0.344°C, the percentage dissociation of NaCl in the solution is
   (A) 75% (B) 80%
   (C) 85% (D) 90%

Paragraph II

Colligative properties of solutions depend only on the total number of solute particles present in solution. In the ionization of electrolytes, more particles are present per unit in solution due to dissociation. The colligative properties of such electrolytes are correlated with the number of particles by means of a factor called van't Hoff factor, denoted by *i*.

6. The van't Hoff factor for NaCl is 1.4. The degree of dissociation is
   (A) 40% (B) 100%
   (C) 90% (D) 60%

7. The ratio of elevation of boiling point for NaCl solution to that for sugar of same concentration is
   (A) 1 (B) 2
   (C) 3 (D) 0.5

8. A 0.01 M solution of $K_2[Fe(CN)_6]$ is 50% dissociated at 27°C. Then the osmotic pressure of solution will be
   (A) 0.02 atm (B) 0.61 atm
   (C) 0.78 atm (D) 1.29 atm

Paragraph III

A solution is said to be ideal if each of its components obey Raoult's law for the entire composition range. The law states that the vapor pressure of any component in the solution depends on the mole fraction of that component in the solution and vapor pressure of that component in the pure state. Solutions are non-ideal if they do not obey Raoult's law over the entire composition range. The vapor pressure of the solution is either higher or lower than that predicted by Raoult's law. Depending on the type of deviation from ideal behavior, non-ideal solutions may be classified as showing negative deviation (lower vapor pressure than predicted) or positive deviation (higher vapor pressure than predicted). However, in either case, corresponding to a particular composition, they form constant boiling mixtures called azeotropes.

9. Which of the following mixtures do you expect will show positive deviation from Raoult's law?
(A) Benzene + Acetone
(B) Benzene + Chloroform
(C) Benzene + Carbon tetrachloride
(D) Benzene + Ethanol

10. An azeotropic solution of two liquids has boiling point higher than either of the two liquids when it
(A) is saturated.
(B) shows a negative deviation from Raoult's law.
(C) shows a positive deviation from Raoult's law.
(D) shows no deviation from Raoult's law.

11. A solution has a 1:4 mole ratio of heptane to hexane. The vapor pressures of the pure hydrocarbons at 20°C are 440 mm Hg for heptane and 120 mm Hg for hexane. The mole fraction of pentane in the vapor phase would be
(A) 0.200 (B) 0.478
(C) 0.549 (D) 0.786

Integer Answer Type

The answer is a **non-negative integer**.

1. van't Hoff factor of an electrolyte A_2B_3 assuming that it ionizes 75% in the solution is __________.

2. At 20°C, the osmotic pressure of urea solution is 400 mm Hg. The solution is diluted and the temperature is raised to 35°C, when the osmotic pressure is round to be 105.3 mm Hg. Determine extent of dilution.

3. An aqueous: solution containing 5% by weight of urea and 10% by weight of glucose. What will be the ΔT_f of solution? (Given that K_f for H_2O is 1.86°C kg mol^{-1}.)

4. The van't Hoff factor *i* for the species $[Fe(H_2O)_2(CN)_5]NO_3{\cdot}2H_2O$ is __________.

5. The freezing point of an aqueous solution of KCN containing 0.189 mol kg^{-1} was –704°C. On adding 0.095 mol of $Hg(CN)_2$. The freezing point of the solution became –0.53°C. What will be new "*i*" factor of the resulting solution? (Assuming that $Hg(CN)_2$ and KCN are produced the complex.)

6. A complex is represented as $CoCl_3{\cdot}xNH_3$. Its 0.1 molal solution in aqueous solution shows $\Delta T_f = 0.558$°C. K_f for H_2O is 1.86 K $molal^{-1}$. Assuming 100% ionization of complex and coordination number of Co as 6, find the value of *x*.

7. The molal lowering of vapor pressure of a liquid is 1.008 mm Hg at 25°C in a very dilute solution containing non-volatile solute. The vapor pressure of liquid at 25°C is Z × 10 mm Hg. The value of *Z* is. (Mol. wt. of liquid = 18 g mol^{-1})

8. The depression in freezing point for 1 M urea, 0.5 M glucose, 1 M NaCl and 1 M K_2SO_4 are in the ratio *x*:1:*y*:*z*. The value of *x* + *z* is __________.

9. The elevation in boiling point for 0.3 molal $Al_2(SO_4)_3$ solution as compared to elevation in boiling point of 0.1 molal solution of Na_2SO_4 is __________ times.

Matrix–Match Type

1. Match the solutions with their characteristics.

Column I	Column II
(A) CH_3COOH in H_2O	(p) Neither association nor dissociation
(B) CH_3COOH in benzene	(q) When a non-volatile solute is added
(C) Polymer in water	(r) Molecular mass observed greater than molecular mass actual
(D) Vapor pressure of a liquid decreases	(s) $\Delta T_{f(obs)} > \Delta T_{f(calc)}$
	(t) van't Hoff factor, $i > 1$

2. For a solution containing 25% ethanol, 25% acetone, 25% acetic acid and 25% water, match the mole fractions of the substances with their values.

Column I	Column II
(A) Mole fraction of ethanol	(p) 0.500
(B) Mole fraction of acetone	(q) 0.150
(C) Mole fraction of acetic acid	(r) 0.155
(D) Mole fraction of water	(s) 0.195

3. Match the columns I and II.

Column I	Column II
(A) Azeotropes	(p) Molality
(B) A mixture of $CHCl_3$ and benzene shows	(q) Intermolecular attraction negative deviation from ideal behavior
(C) The ratio of observed molecular mass to theoretical molecular mass	(r) van't Hoff factor
(D) The number of moles of solute dissolved in 1000 g of solvent	(s) Solutions with same composition in vapor and liquid phase
	(t) Constant boiling mixtures

4. Match the columns I and II using the information below:
ΔH_{fus} = Molar heat of fusion of ice; L_{fus} = Latent heat of fusion of ice (g^{-1})
ΔH_{vap} = Molar heat of vaporization of water; L_{vap} = Latent heat of vaporization of water (g^{-1})

Column I	Column II
(A) Molal depression constant of water	(p) $\dfrac{18\times 373\times 373\times R}{1000\Delta H_{\text{vap}}}$
(B) Molal elevation constant of water	(q) $\dfrac{373\times 373\times R}{1000 L_{\text{vap}}}$
(C) ΔT_f of solution containing 9.0 g of glucose in 50 g of water	(r) $\dfrac{18\times 273\times 273\times R}{1000\Delta H_{\text{fus}}}$
(D) ΔT_b of solution containing −3.0 g of urea in 50 g of water	(s) $\dfrac{273\times 273\times R}{1000\Delta H_{\text{fus}}}$
	(t) K_f

5. For a 5% solution of H_2SO_4 ($\rho = 1.01$ g mL^{-1}), match the quantities with their values.

Column I	Column II
(A) Molarity of the solution	(p) 0.537
(B) Molality of the solution	(q) 0.0096
(C) Mole fraction of H_2SO_4	(r) 0.05
(D) Mass fraction of H_2SO_4	(s) 0.515

6. Match the columns I and II. Consider constant pressure of 1 atm.

Column I	Column II
(A) Mixture of two immiscible liquids	(p) Composition dependent
(B) Solution of two miscible liquids	(q) Constant. Independent to the relative amounts of the liquids
(C) Maximum boiling point azeotrope	(r) Constant along with composition
(D) Minimum boiling point azeotrope	(s) Constant, composition of solution and vapor being identical
	(t) Can be basis of separation of liquid from mixture

ANSWERS

Review Questions

1. The formula must be PCl_3. The structure is trigonal pyramidal. Molarity = 0.404 M.
2. Due to the tendency for all systems to proceed spontaneously towards a state of randomness.
3. The temperature decreases as the solute dissolves. Lattice energy is numerically larger.
8. The tendency towards randomness and the new forces of attraction between solute and solvent molecules
9. Al^{3+} ion has the larger hydration energy.
10. 350 g
17. The molarity will be greater than 1.0.
22. $i = 1$ for non-dissociating molecular solutes; $i > 1$ indicates dissociation of the solute; $i < 1$ indicates association of the solute; $i = 0.5$ indicates the formation of dimers.
23. The one with the lower molarity.
26. 10% glucose
27. Na_2CO_3

Numerical Problems

1. –0.15°C
2. 0.25
3. 0.444
4. 76.95 g
5. 99.2 %
6. 9.9%
7. $\dfrac{i-1}{n-1}$
8. 37.31 atm
9. 800 g
10. 120.0 g mol^{-1}
11. $i = 1/2$
12. 80%
13. $i = 2$
14. $i = 2$
15. –0.2°C
16. **(a)** (ii) < (iv) < (i) < (iii)
    (b) (iii) < (i) < (ii)
    (c) (iv) < (v) < (i) < (ii) < (iii)
17. 179.1 g mol^{-1}
18. 0.25

19. 0.604 mol solute per mole of benzene **20.** 100.256°C **21.** 72 mm Hg **22.** $\Pi_2 > \Pi_1 > \Pi_3$

23. 68.4 g mol^{-1} **24.** 80% **25.** 1:2:3 **26.** 101.04°C

Additional Objective Questions

Single Correct Choice Type

1. (C) **2.** (B) **3.** (B) **4.** (B) **5.** (B)
6. (A) **7.** (A) **8.** (B) **9.** (D) **10.** (B)
11. (B) **12.** (C) **13.** (D) **14.** (B) **15.** (B)
16. (D) **17.** (C) **18.** (C) **19.** (B) **20.** (B)
21. (A) **22.** (B) **23.** (B) **24.** (A) **25.** (B)
26. (B) **27.** (C) **28.** (B) **29.** (B) **30.** (B)
31. (B) **32.** (D) **33.** (A) **34.** (A) **35.** (A)
36. (B) **37.** (D) **38.** (C) **39.** (C) **40.** (C)
41. (B) **42.** (D) **43.** (A) **44.** (D) **45.** (A)
46. (C) **47.** (B) **48.** (B) **49.** (D) **50.** (B)
51. (B) **52.** (B) **53.** (C) **54.** (D) **55.** (A)
56. (C) **57.** (A) **58.** (A) **59.** (D) **60.** (D)
61. (A) **62.** (A) **63.** (C) **64.** (D) **65.** (A)
66. (A) **67.** (B) **68.** (B) **69.** (C) **70.** (D)
71. (C) **72.** (B) **73.** (C) **74.** (A) **75.** (C)
76. (A) **77.** (A) **78.** (B) **79.** (A) **80.** (B)
81. (A) **82.** (B) **83.** (D) **84.** (C) **85.** (A)
86. (B) **87.** (B) **88.** (D) **89.** (D) **90.** (C)
91. (D)

Multiple Correct Choice Type

1. (A, B, C, D) **2.** (A, B, D) **3.** (C, D) **4.** (A, B) **5.** (A, D)
6. (A, B) **7.** (A, C) **8.** (B, D) **9.** (A, B, C) **10.** (A, D)
11. (A, C) **12.** (A, B, C) **13.** (A, C, D) **14.** (A, C, D) **15.** (A, B)
16. (A, B) **17.** (A, C, D) **18.** (B, D) **19.** (A, C, D) **20.** (A, C)

Assertion–Reasoning Type

1. (B) **2.** (C) **3.** (A) **4.** (A) **5.** (D)
6. (A) **7.** (D) **8.** (C) **9.** (B) **10.** (A)

Comprehension Type

1. (D) **2.** (D) **3.** (C) **4.** (C) **5.** (C)
6. (A) **7.** (B) **8.** (B) **9.** (A) **10.** (B)
11. (B)

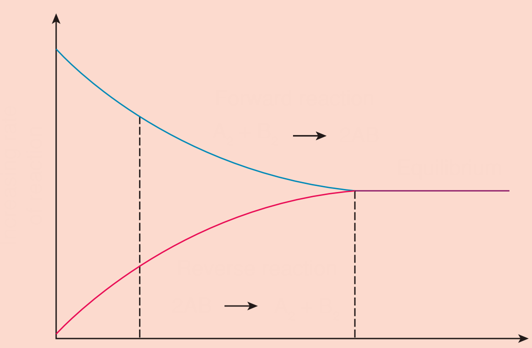
Integer Answer Type

1. (4) **2.** (4) **3.** (3) **4.** (2) **5.** (3)
6. (5) **7.** (6) **8.** (8) **9.** (5)

Matrix–Match Type

1. A → (s, t); B → (r); C → (p); D → (q)
2. A → (s); B → (r); C → (q); D → (p)
3. A → (s, t); B → (q); C → (r); D → (p)
4. A → (r, t); B → (p); C → (r, s, t); D → (p, q)
5. A → (s); B → (p); C → (q); D → (r)
6. A → (q, t); B → (p, t); C → (r, s); D → (r, s)

9



A_2, B_2 and AB in equilibrium

Contents

9.1 Physical Equilibria
9.2 Chemical Equilibria – Dynamic Equilibrium
9.3 Law of Chemical Equilibrium and Equilibrium Constant
9.4 Homogeneous and Heterogeneous Equilibria
9.5 Applications of Equilibrium Constants
9.6 Gibbs Energy Change and Chemical Equilibrium
9.7 Simultaneous Equilibrium
9.8 Le Chatelier's Principle and Factors Affecting Equilibria

An equilibrium system is the system in which the macroscopic properties of the system, such as temperature, pressure, concentration, etc., do not change. Any increase in these properties is balanced by a decrease in that property within the system. There are two kinds of equilibrium.

1. **Physical equilibrium:** This equilibrium exists between different physical states or when phases undergo transition. These phase transformations take place when energy is added to or removed from the system and can be of the following types:
   - **(a)** the solid–liquid equilibrium;
   - **(b)** the liquid–gas equilibrium;
   - **(c)** the solid–gas equilibrium;

   For example, the evaporation of a liquid in a closed container is an example of a system in equilibrium. The system is said to reach a **state of equilibrium** when the number of molecules leaving the liquid surface becomes equal to the number of molecules returning back from vapor phase. The equilibrium can be represented as follows.

   $$\text{Liquid state} \rightleftharpoons \text{Vapor phase}$$

2. **Chemical equilibrium:** Consider a chemical reaction taking place in a closed container. The reactants first react to form products. With the passage of time, the concentration of reactants decreases while that of products increases, till a stage of **chemical equilibrium** is reached where there is no further change in concentrations of either reactants or products. This state of equilibrium is also not static, instead a chemical equilibrium is a **dynamic system** in which two or more opposing chemical reactions are going on at the same time and at the same rate.

The chemical reactions that do not go to completion and can occur in either direction are called **reversible reactions**. When the rate of the forward reaction is exactly equal to the rate of the reverse reaction, a condition of chemical equilibrium exists. The mixture of reactants and products in the equilibrium state is called an **equilibrium mixture**. The nature of the equilibrium mixture is determined by the extent of reaction as follows:

(a) The reaction has almost proceeded to completion and very small concentrations of reactants are left, which are undetectable by experimental methods.

(b) The concentrations of reactants and products are comparable.

(c) The reaction has proceeded only to a small extent, so amount of products is small and reactants are predominant.

In this chapter, we will learn about characteristics of systems in chemical equilibrium. However, before that we will first look at equilibrium involving physical changes.

9.1 | PHYSICAL EQUILIBRIA

The physical equilibrium can be attained in closed system. The rate of change between the phases is the same at equilibrium. Thus, the equilibrium is stable yet dynamic because two opposing processes take place simultaneously.

Solid–Liquid Equilibrium

Consider the solid–liquid equilibrium in water and ice in a glass containing ice cubes:

$$\text{Ice (solid)} \rightleftharpoons \text{Water (liquid)}$$

The ice cubes melt to form water and some water in contact with ice may freeze back to ice. A dynamic equilibrium exists at 0°C (273 K). At the surface of ice, the molecules of ice convert into water and the liquid water molecules in close contact with ice are converted back to ice. The equilibrium is disturbed as the temperature rises and the ice eventually melts into water. However, if ice cubes and water are kept at 0°C in an insulated container at atmospheric pressure, no exchange of heat takes place between the container and the surroundings. The mass of ice and water continues to be the same because these two opposing processes take place at the same time and at the same rate. A state of equilibrium is obtained where the mass of ice and water do not change with time and temperature remains constant. This temperature at which solid and liquid phases coexist in equilibrium is called the melting point of solid or the freezing point of the liquid.

Note: The temperature at which the substance melts at 1 atm pressure is known as the normal melting point of the solid (or normal freezing point of the liquid). The energy required to melt one mole of a solid is called **molar heat of fusion** and is usually expressed in kilojoules.

Liquid–Vapor Equilibrium

Consider liquid–vapor equilibrium in conversion of water into its vapor. This phase change when a liquid is transformed into a gas is known as **evaporation** or **vaporization**. On heating, the kinetic energy of the molecules increases, and hence more molecules can escape the surface of the liquid.

Consider a transparent container with a U-shaped tube carrying mercury (manometer). The air inside the container is dried and some water is added to the vessel. Initially, the mercury levels in the U-shaped manometer tube are the same. After some time, the amount of water in the container is reduced and the mercury rises in the right side of the manometer tube. Eventually, the mercury level stabilizes and no further increase is observed. This happens because initially, when water is introduced into the container, no vapor phase exists. When the process of **evaporation** or **vaporization** starts, the water molecules begin to leave the liquid surface and a vapor phase is established. Once a fair amount of vapor is present, a measureable vapor pressure develops and the mercury rises in the manometer. As the number of water molecules in vapor phase increase, some of them strike the liquid surface and are converted back to liquid phase and the process is known as **condensation**. After sometime, the rate of evaporation becomes equal to the rate of condensation and a state of dynamic equilibrium is achieved (Fig. 9.1). The equilibrium can be represented as

$$\text{Water (liquid)} \rightleftharpoons \text{Water (vapor)}$$

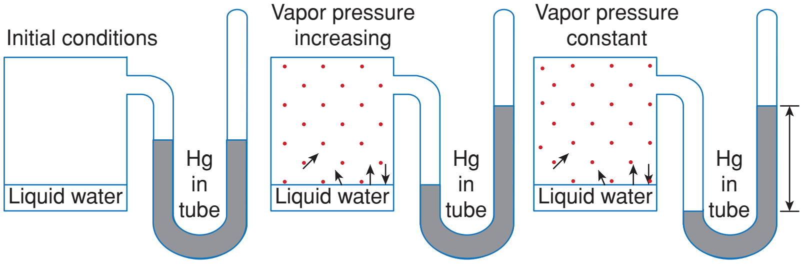


Figure 9.1 Measurement of equilibrium vapor pressure of water.

The vapor pressure measured when a dynamic equilibrium exists between condensation and evaporation is known as **equilibrium vapor pressure** (or just the vapor pressure of water). The vapor pressure of a liquid increases with increase in temperature and when it becomes equal to the external pressure, the liquid begins to boil. The vapor pressure is specific for a substance.

Note: For any pure liquid at 1 atm pressure, the temperature at which the vapor pressure becomes equal to the external pressure is known as the normal **boiling point** of the liquid. For water, the boiling point at 1 atm (or 1.013 bar) in a closed container is 100°C. The energy required to vaporize one mole of liquid is known as molar heat of vaporization and is usually expressed in kilojoules.

Solid–Vapor Equilibrium

The process by which a solid is directly converted into vapor state is known as **sublimation**. Consider solid–vapor equilibrium in sublimation of iodine. When iodine is placed in a closed vessel, the vessel gets filled with violet vapors of iodine after sometime. The intensity of the color increases for some time and then becomes constant. This corresponds to the state of dynamic equilibrium where the rate of conversion of solid iodine to vapor is the same as the rate at which iodine vapors condense back to solid iodine.

$$\text{Iodine (solid)} \rightleftharpoons \text{Iodine (vapor)}$$

Note: The energy required to sublime one mole of a solid is known as molar energy of sublimation and is usually expressed in kilojoules.

Equilibrium in Dissolution of Solids and Gases in Liquids and Henry's Law

The dissolution of solids or gases in liquids suggests the existence of some kind of equilibrium between the dissolved substance (gas or solid) and the liquid.

1. **Solids in liquids:** The amount of solid that dissolved in a liquid varies with temperature. The amount of substance that dissolves in a given amount of solvent is known as its **solubility** at that temperature. The change of temperature will alter the solubility of a solid in a liquid. When the maximum amount of solid is dissolved in a given amount of liquid at a specific temperature, the solution is said to be a **saturated solution**. The concentration of the saturated solution depends on temperature. The dynamic equilibrium that exists between sugar molecules dissolved in the solution and molecules in solid form in a saturated solution is as follows:

$$\text{Sugar (solution)} \rightleftharpoons \text{Sugar (solid)}$$

2. **Gases in liquids:** The fizzing sound that results when a sealed bottle or can of aerated drink is opened can be explained on the basis of difference in solubility of gases in liquids with change in pressure. At a given pressure,

equilibrium exists between the gas (carbon dioxide in this case) molecules dissolved in the liquid and those in gaseous state. This can be represented as

$$CO_2\,(gas) \rightleftharpoons CO_2\ (in\ solution)$$

The amount of gas dissolved is determined by the pressure. On opening the can, the pressure increases to the atmospheric pressure, the gas dissolved in solution decrease and escapes; a new equilibrium is established for the new pressure conditions. At equilibrium, the amount of gas dissolved in a given mass of liquid at any temperature is proportional to the pressure of the gas above the liquid and this is known as **Henry's law**.

Henry's law (also called the **Pressure–Solubility law**) states that *the concentration of a gas dissolved in a given volume in a liquid at any given temperature is directly proportional to the partial pressure of the gas over the solution.*

$$C_{\text{gas}} = K_{\text{H}} p_{\text{gas}} \qquad (K_{\text{H}}\ \text{is constant}) \tag{9.1}$$

where C_{gas} is the concentration of the gas and p_{gas} is the partial pressure of the gas above the solution. The proportionality constant, K_{H}, called the Henry's law constant, is unique to each gas. The equation is true only at low concentrations and pressures and for gases that do not react with the solvent. An alternate (and commonly used) form of Henry's law is

$$\frac{C_1}{p_1} = \frac{C_2}{p_2} \tag{9.2}$$

Characteristics of Physical Equilibria

The characteristic feature of physical equilibria corresponding to phase transformations and dissolution of solids and gases in liquids are as follows.

1. For a liquid–vapor equilibrium, the vapor pressure is constant at a given temperature.
2. For a solid–liquid equilibrium, at atmospheric pressure, the two phases coexist at one temperature which is known as the melting point of solid or freezing point of the liquid.
3. For dissolution of solids in liquids, the solubility is constant at a given temperature.
4. For dissolution of gases in liquids, the concentration of gas in the solution is proportional to the pressure over the liquid, at a given temperature.

The general features of systems in physical equilibrium are as follows:

1. Equilibrium can be observed only in closed system at a given temperature.
2. At the macroscopic level, there is no measurable change in the properties of the system.
3. At molecular level, two equal and opposite processes take place at the same rate, so the equilibrium is dynamic in nature.
4. The physical equilibrium is characterized by constant value of any one parameter, such as concentration and pressure, at constant temperature. The magnitude of these quantities will determine the extent of physical change the system will undergo before it reaches the stage of equilibrium.

9.2 | CHEMICAL EQUILIBRIA – DYNAMIC EQUILIBRIUM

Chemical reactions are reversible in nature to some extent and only a few reactions proceed only in one direction. Consider the following reversible reaction which is carried out in a closed container:

$$A + B \rightleftharpoons C + D$$

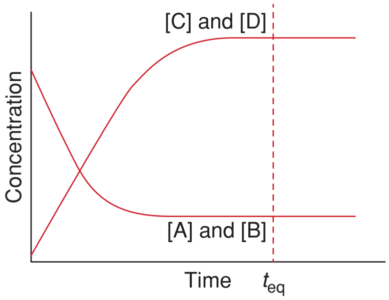


Figure 9.2 Variation in the concentration of species present in the reaction $A + B \rightleftharpoons C + D$ system as equilibrium is approached.

Initially, the reactants undergo forward reaction to form products. However, once some products are formed the reverse reaction also becomes feasible. As time progresses, a decrease in the rate of forward reaction is observed and the rate of reverse reaction increases. But gradually, the system is said to be in *chemical equilibrium* when the rate of forward reaction is equal to the rate of backward reaction. The state of chemical reaction when the concentrations of the reactants and products do not change with time is called **equilibrium state**. In this state, the measurable properties of the system such as pressure, density, concentration or color do not undergo any noticeable change with time under the given set of condition. The state of equilibrium is **dynamic** because two processes (a forward reaction in which reactants give product(s) and a backward or reverse reaction in which product(s) combine to give the original reactants) are occurring simultaneously, but at the same rate. As a result, the concentration of reactants and products remains constant (Fig. 9.2).

Note: Chemical equilibrium can be attained only in a closed system because in an open system, where the products are removed from the reaction mixture, the reaction would continue till one of the reactants is used up completely.

For graphical illustration (Fig. 9.3) of a reversible reaction and the point of equilibrium, consider the following reversible reaction which is carried out in a closed container:

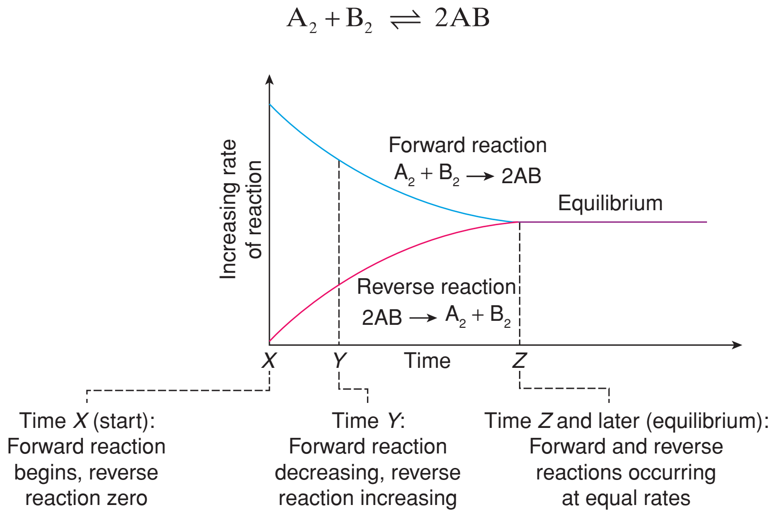


Figure 9.3 A_2, B_2 and AB in equilibrium.

Based on this graphical representation and above observations, the characteristic features of chemical equilibrium state can be summarized as follows:

1. It is established in a closed system.
2. It is dynamic in nature.
3. At equilibrium state, the rate of forward and backward reactions is the same.
4. At equilibrium state, the concentration of the reactants and products remains constant.
5. It can be attained either from the reactants or the products side. At equilibrium, each reactants and product has fixed concentration, irrespective of which side the reaction is approached.
6. It is not affected by the presence of a catalyst. However, the equilibrium state can be attained in lesser time by use of positive catalyst.

The reaction between H_2 and I_2 provides another example of chemical equilibrium (Fig. 9.4):

$$H_2(g) + I_2(g) \xrightleftharpoons{700\text{ K}} 2HI(g)$$

This equation represents the condition if the reaction were 100% complete, 2.00 mol HI would be formed, and no H_2 and I_2 would be left unreacted. When the equation is 79% complete, we have the following equation:

$$\underset{0.21\text{ mol}}{H_2(g)} + \underset{0.21\text{ mol}}{I_2(g)} \xrightleftharpoons{700\text{ K}} \underset{1.58\text{ mol}}{2HI(g)}$$

This equation represents the actual equilibrium attained starting with 1.00 mol each of H_2 and I_2. It shows that the forward reaction is only 79% complete (Fig. 9.4).

This reversible reaction also shows all the characteristics of chemical equilibrium. We can attain the equilibrium by starting with HI. Initially, the concentration of HI will decrease and that of H_2 and I_2 will increase until the equilibrium is reached and the composition of the mixture becomes constant.

Dynamic nature of equilibrium can be explained on the basis of molecular kinetic theory. The molecules of reactants are in constant motion and collide with one another with sufficient energy and proper orientation to break bonds and form new ones that lead to formation of products. Once the products are formed, the product molecules collide with each other and bonds are broken and formed to yield back the reactants. In the initial stage of reaction, the concentration of reactant molecules is more, so their bonds are broken predominantly to form products. However, as the concentration of product molecules increases, their collisions and bond breaking and making also become effective. Eventually, a state of equilibrium is reached where the two rates become equal.

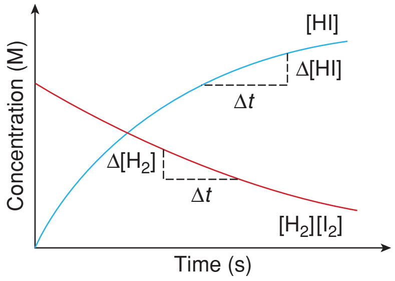


Figure 9.4 Plot of molar concentration vs. time for formation of HI.

9.3 | LAW OF CHEMICAL EQUILIBRIUM AND EQUILIBRIUM CONSTANT

Law of Mass Action

According to **law of mass action**, the rate of a reaction is proportional to the product of effective concentration of the reacting species (active masses), each raised to a power which is equal the corresponding stoichiometric number of the substance in the balanced chemical equation.

Consider the gaseous reaction of hydrogen with iodine to form hydrogen iodide.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

The fraction used to calculate the values of equilibrium concentrations

$$\frac{[HI]^2}{[H_2][I_2]}$$

is called the **mass action expression**. Now consider a general reversible reaction $A + B \rightleftharpoons C + D$. If the active masses of reactants and products are [A] [B] [C] [D], respectively, then according to law of mass action:

$$\text{Rate of forward reaction} \propto [A][B] = k_f[A][B]$$
$$\text{Rate of backward reaction} \propto [C][D] = k_b[C][D]$$

where k_f and k_b are the rate constants for the forward and backward reactions. At equilibrium, the rates of forward and backward reaction become equal, so

$$k_f[A][B] = k_b[C][D] \Rightarrow \frac{k_f}{k_b} = \frac{[C][D]}{[A][B]} \qquad (9.3)$$

Equation (9.3) is called law of **chemical equilibrium** or the **equilibrium law**. According to this law, the rate of a reaction is proportional to the product of effective concentration of the reacting species, each raised to a power that is equal the corresponding stoichiometric number of the substance in the balanced chemical equation. The constant K_C, which characterizes this equilibrium system, is called the **equilibrium constant** (the subscript C because we write the mass action expression using molar concentrations).

Let us now try to understand the effect of change of concentration of one of the reactants on the equilibrium expression. In the above-stated reversible reaction, if the concentration of B is increased, the following results are observed:

1. The rate of the reaction to the right (forward) increases. This rate is proportional to the concentration of A times the concentration of B.
2. The rate to the right becomes greater than the rate to the left.

3. Reactants A and B are used faster than they are produced; C and D are produced faster than they are used.
4. After a period of time, rates to the right and left become equal, and the system is again in equilibrium.
5. In the new equilibrium, the concentration of A is less and the concentrations of B, C and D are greater than in the original equilibrium.

Applying this change in concentration to the equilibrium reaction mixture of 1.00 mol of hydrogen and 1.00 mol of iodine, we find that, when an additional 0.20 mol I_2 is added, the yield of HI (based on H_2) is 85% (1.70 mol) instead of 79%. Here is how the two systems compare after the new equilibrium mixture is reached:

Initially, $[H_2]$ = decreases, $[I_2]$ = increase and [HI] = decreases.

At equilibrium,

Original Equilibrium	1.00 mol H_2 + 1.00 mol I_2	Yield: 79% HI	Equilibrium mixture contains: 1.58 mol HI, 0.21 mol H_2, 0.21 mol I_2
New Equilibrium	1.00 mol H_2 + 1.20 mol I_2	Yield: 85% HI (based on H_2)	Equilibrium mixture contains: 1.70 mol HI, 0.15 mol H_2, 0.35 mol I_2

Analyzing this new system, we see that when 0.20 mol I_2 is added, the equilibrium shifts to the right to counteract the increase in I_2 concentration. Some of the H_2 reacts with added I_2 and produces more HI, until an equilibrium mixture is established again. When I_2 is added, the concentration of I_2 increases, that of H_2 decreases and that of HI increases. In the new system, $[H_2]$ decreases, $[I_2]$ increases and [HI] increases.

Equation (9.3) can be written for the hydrogen–iodine reaction as follows:

$$K = \frac{[\mathrm{HI(g)}]^2}{[\mathrm{H_2(g)}][\mathrm{I_2(g)}]}$$

Now consider a general reversible reaction:

$$a\mathrm{A} + b\mathrm{B} \rightleftharpoons c\mathrm{C} + d\mathrm{D}$$

or

$$K = \frac{[\mathrm{C}]^c[\mathrm{D}]^d}{[\mathrm{A}]^a[\mathrm{B}]^b} \tag{9.4}$$

The equilibrium constant may be defined as the ratio between the product of the molar concentrations of the products to that of the product of molar concentrations of reactants, with each concentration term raised to power equal to stoichiometric coefficient in the balanced chemical equation.

Equilibrium Constants K_p and K_c

For gaseous reactions, since gas pressures are more conveniently measured, the equilibrium law expressions for gaseous reactions are written using partial pressures instead of molar concentrations. Thus, the concentration or active masses in Eq. (9.4) can be replaced by partial pressures to give

$$K_p = \frac{[p_\mathrm{C}]^c \times [p_\mathrm{D}]^d}{[p_\mathrm{A}]^a \times [p_\mathrm{B}]^b} \tag{9.5}$$

where p_A, p_B, p_C and p_D the partial pressures of A, B, C and D, respectively and K_p is called pressure equilibrium constant.

Consider the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$. The equilibrium law expression is

$$K_p = \frac{p_{\mathrm{NO_2}}^2}{p_{\mathrm{N_2O_4}}}$$

where $p_{\mathrm{NO_2}}$ and $p_{\mathrm{NO_2}}$ are the partial pressures of NO_2 and N_2O_4 at equilibrium.

Relationship between K_p and K_C

The two equilibrium constants can be related using the ideal gas equation as follows:

$$pV = nRT$$

or

$$p = \frac{n}{V} \times RT = CRT$$

as number of moles per unit volume is equal to concentration.

Consider the reaction $a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$. Substituting this value of p in Eq. (9.7), we get

$$K_p = \frac{[C]^c [RT]^c \times [D]^d [RT]^d}{[A]^a [RT]^a \times [B]^b [RT]^b} = \frac{[C]^c \times [D]^d}{[A]^a \times [B]^b} \times RT^{(c+d)-(a+b)}$$

where $(c + d) - (a + b) = \Delta n_g$, that is, number of gaseous moles of products – number of gaseous moles of reactants. Therefore,

$$K_p = K_C \times (RT)^{\Delta n_g} \tag{9.6}$$

From Eq. (9.6), we have the following observations:

1. When the number of moles of products is equal to that of the reactants, that is, $\Delta n = 0$; $K_p = K_C$.
2. When the number of moles of products is more than that of the reactants, that is, $\Delta n > 0$; $K_p > K_C$.
3. When the number of moles of products is less than that of reactants, that is, $\Delta n < 0$, $K_p < K_C$. Here $\Delta n = -1$.

The value of equilibrium constant depicts the following characteristic features:

1. It is constant for a reaction at a given temperature and varies with change in temperature. For an endothermic reaction, it increases as the temperature is increased; and for an exothermic reaction it decreases as the temperature is increased.
2. It is independent of the original concentration of reactants and presence of the catalyst.
3. It is independent of the direction from which equilibrium is attained and the nature and number of steps involved in the reaction.
4. When it is large, the equilibrium of the reaction lies towards the products side.
5. For the reverse reaction, it is equal to the inverse of value for the forward reaction.

Note: The expression for equilibrium constant is derived based on thermodynamics, so technically each concentration term must be divided by its standard state value before it is put in the expression. This makes the value of equilibrium expression unitless. For substances in solution, the standard state is one molar concentration, so each concentration must be divided by 1 mol L^{-1} concentration, which does not alter the expression for equilibrium constant, if the concentrations are molarities. For gases, the standard state is 1 bar, so concentration of each gas is divided by concentration at that pressure or partial pressure of each gas must be divided by 1 bar. However, for the sake of simplicity these values are not included in the expression for equilibrium constant.

Units of K_p and K_C

Concentration is generally expressed in moles per liter and pressure in atmospheres. The units of K_p and K_C depend on the stoichiometry of the reaction. Consider the following cases:

Case 1: When the total number of moles of reactants and products are equal. For example, $H_2(g)+I_2(g) \rightleftharpoons 2HI(g)$

$$K_C = \frac{[HI]^2}{[H_2][I_2]} = \frac{(\text{mol L}^{-1})^2}{(\text{mol L}^{-1})\times(\text{mol L}^{-1})} \Rightarrow \text{No units}$$

$$K_p = \frac{[p_{HI}]^2}{p_{H_2}\,p_{I_2}} = \frac{(\text{atm})^2}{(\text{atm})\times(\text{atm})} \Rightarrow \text{No units}$$

Thus, for such reactions, K_C and K_p are without any units.

Case 2: When the total number of moles of reactants and products are unequal. For example, $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

$$K_C = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(\text{mol L}^{-1})^2}{(\text{mol L}^{-1})} = \text{mol L}^{-1}$$

$$K_p = \frac{p^2_{NO_2}}{p_{N_2O_4}} = \frac{(\text{atm})^2}{(\text{atm})} = \text{atm}$$

In such reactions, K_C will have units $(\text{mol L}^{-1})^{\Delta n}$ and K_p will have the units $(\text{atm})^{\Delta n}$ where Δn = total number of moles of products – total number of moles of reactants.

Solved Example 9-1

At 500 °C, the reaction between N_2 and H_2 to form ammonia has $K_C = 6.0 \times 10^{-2}$. What is the numerical value of K_p for the reaction $N_2(g)+3H_2(g) \rightleftharpoons 2NH_3(g)$?

Solution

The tool we need to convert between K_p and K_C is

$$K_p = K_C(RT)^{\Delta n} \qquad (1)$$

In the discussion above, we saw all we need now are appropriate values of R and T. (When used to stand for temperature, a capital letter T in an equation always means the absolute temperature.) Next, we must choose an appropriate value for R. Referring back to equation ($p = CRT$) and this is the *only* value of R that can be used in Eq. (1). We can see that $\Delta n = -2$ for this reaction. The temperature T must be expressed in kelvins and if the partial pressures are expressed in atm and the concentration in mol L^{-1} the only value of R that includes all of these units (L, mol, atm and K) is $R = 0.0821$ L atm mol^{-1} K^{-1}.

From the given data, then, we have $K_C = 6.0 \times 10^{-2}$, $\Delta n = -2$ mol, $T = 500 + 273 = 773$ K and $R = 0.0821$ L atm $\text{mol}^{-1}K^{-1}$. Substituting these into the equation for K_p gives

$$K_p = (6.0\times10^{-2})\times[(0.0821)\times(773)]^{-2}$$
$$= (6.0\times10^{-2})/(63.5)^2 = 1.5\times10^{-5}$$

In this case, K_p has a numerical value quite different from that of K_C.

Solved Example 9-2

The equilibrium constant K_C for the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ is 0.5 $L^2\text{mol}^{-2}$ at 400 K. Find K_p, given that $R = 0.082$ l atm $K^{-1}\text{mol}^{-1}$.

Solution

The given equilibrium is $N_2(g)+3H_2(g) \rightleftharpoons 2NH_3(g)$ where $\Delta n = 2 - (1 + 3) = -2$. Substituting the values of Δn, K_C, R and T we get K_p as

$$K_p = K_C(RT)^{\Delta n} = 0.5\times(0.082\times400)^{-2} = 4.636\times10^{-4}\ \text{atm}^2$$

Solved Example 9-3

Calculate the K_C and K_p for the following reactions and also deduce the relationship between K_C and K_p.

(a) $2SO_2(g)+O_2(g)\rightleftharpoons 2SO_3(g)$

(b) $\frac{1}{2}N_2(g)+\frac{3}{2}H_2(g)\rightleftharpoons NH_3(g)$

Solution

(a) $2SO_2(g)+O_2(g)\rightleftharpoons 2SO_3(g)$ applying law of mass action,

$$K_C=\frac{[SO_3]^2}{[SO_2]^2[O_2]} \quad \text{and} \quad K_p=\frac{p^2_{SO_3}}{p^2_{SO_2}\times p_{O_2}}$$

We know that, $K_p=K_C(RT)^{\Delta n}$ where

$$\Delta n=2-(2+1)=-1\Rightarrow K_p=\frac{K_C}{RT}$$

(b) $\frac{1}{2}N_2(g)+\frac{3}{2}H_2(g)\rightleftharpoons NH_3(g)$

$$K_C=\frac{[NH_3]}{[N_2]^{1/2}[H_2]^{3/2}} \quad \text{and} \quad K_p=\frac{p_{NH_3}}{p^{1/2}_{N_2}\times p^{3/2}_{H_2}}$$

Now, $K_p=K_C(RT)^{\Delta n}$ where

$$\Delta n=1-\left(\frac{3}{2}+\frac{1}{2}\right)=-1\Rightarrow K_p=\frac{K_C}{RT}$$

Solved Example 9-4

Consider $NH_2COONH_4(s)\rightleftharpoons 2NH_3(g)+CO_2(g)$ in a closed vessel at equilibrium after dissociation. Now, NH_3 is added such that the partial pressure of NH_3 is equal to the original total pressure. Calculate the ratio of the total pressure now to the original total pressure.

Solution

Let the original pressure be p. Then, we have $p_{NH_3}=\frac{2}{3}p$

and $p_{CO_2}=\frac{1}{3}p$

According to the reaction, we have

$$K_p=p^2_{NH_3}\times p_{CO_2}=\left(\frac{2}{3}p\right)^2\times\left(\frac{1}{3}p\right)=\frac{4}{27}p^3$$

On adding NH_3, it is given that $p_{NH_3}=\frac{2}{3}p$. So,

$$K_p=p^2_{NH_3}\times p_{CO_2}=p^2p_{CO_2}$$

or $$\frac{4}{27}p^3=p^2\times p_{CO_2}\Rightarrow p_{CO_2}=\frac{4}{27}p$$

Total pressure $=p_{NH_3}+p_{CO_2}=p+\frac{4}{27}p=\frac{31}{27}p$

Therefore, the ratio of total pressure to original pressure is 31/27.

Solved Example 9-5

One of the reaction that takes place in producing steel from iron ore is the reduction of iron (II) oxide by carbon monoxide to give iron metal and CO_2.

$$FeO(s)+CO(g)\rightleftharpoons Fe(s)+CO_2(g) \quad K_p=0.265 \text{ at } 1050\text{ K}$$

What are the equilibrium partial pressures of CO and CO_2 at 1050 K if the initial partial pressures are $p_{CO}=1.4$ atm and $p_{CO_2}=0.80$ atm?

Solution

For this reaction at equilibrium

$$K_p=\frac{p_{CO_2}}{p_{CO}}=0.265\Rightarrow p_{CO_2}=K_pp_{CO}=0.265\,p_{CO}$$

Sum of initial partial pressures $=p_{CO}+p_{CO_2}$

$=1.4\text{ atm}+0.8\text{ atm}$

$=2.2\text{ atm}$

Sum of partial pressures at equilibrium $=p_{CO}+0.265\,p_{CO}$

$=1.265\,p_{CO}$

As there is no change in the number of moles of gaseous components during the reaction, we have

$$1.265p_{CO}=2.2\text{ atm}\Rightarrow p_{CO}=\frac{2.2\text{ atm}}{1.265}=1.74\text{ atm}$$

So, $p_{CO_2}=0.265\times p_{CO}=0.265\times 1.74\text{ atm}=0.46\text{ atm}$

Characteristics of Equilibrium Constant

Let us consider another example of reaction between $ClNO_2$ and NO that eventually reaches equilibrium at a given temperature.

$$ClNO_2(g) + NO(g) \rightleftharpoons NO_2(g) + ClNO(g)$$

No matter what combination of concentrations of reactants and products we start with, the reaction reaches equilibrium when the ratio of the concentrations defined by the equilibrium constant expression is equal to the equilibrium constant for the reaction at the chosen temperature. We can start with a lot of $ClNO_2$ and very little NO, or a lot of NO and very little $ClNO_2$. It does not matter. When the reaction reaches equilibrium, the relationship between the concentrations of the reactants and products described by the equilibrium constant expression will always be the same. At 25°C, this reaction always reaches equilibrium when the ratio of the concentrations is 1.3×10^4.

$$K = \frac{[NO_2][ClNO]}{[ClNO_2][NO]} = 1.3 \times 10^4 \quad \text{(at 25°C)}$$

where K is always reported without units. However, any calculations using K require the concentration of the products and reactants to be in units of molarity (moles liter^{-1}).

If a chemical equation is multiplied by a common factor (n), then the new equilibrium constant should also reflect the change. For example, the equilibrium constant of the following reaction is K_C.

$$4NH_3(g) + 5O_2(g) \rightleftharpoons 5NO(g) + 6H_2O(g)$$

When multiplied by 1/2, the reaction becomes

$$2NH_3(g) + \tfrac{5}{2}O_2(g) \rightleftharpoons 2NO(g) + 3H_2O(g)$$

The new equilibrium constant would be $K'' = K^{1/2}$.

Some characteristics of equilibrium constant based on these observations are listed as follows:

1. For any reaction, K is constant for a specific temperature.

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta H}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

2. It is independent of the initial concentrations of the reactants. For example, for the following reaction in aqueous medium

$$A + B \rightleftharpoons C + D$$
$$K = \frac{[C][D]}{[A][B]}$$

   Now, let us consider if under the following changes, K increases, decreases or remains constant.

   (a) A is added
   (b) B is removed
   (c) Concentration of C is doubled
   (d) Concentration of D is halved
   (e) An inert gas E is added

   K remains constant in all the above cases.

3. It is independent of presence of catalyst and inert materials in the reaction.
4. It is independent of the direction from which the equilibrium is attained.
5. It is dependent on the representation of the reaction.

   (i) For the reactions

$$A \rightleftharpoons B \quad C \rightleftharpoons D$$
$$K_1 = \frac{[B]}{[A]} \quad K_2 = \frac{[D]}{[C]}$$

(a) On addition of reactions *K*'s get multiplied.

$$A + C \rightleftharpoons B + D$$

$$K_3 = \frac{[B][D]}{[A][C]}$$

Here $$K_3 = K_1K_2$$

(b) On subtraction of reactions, *K*'s get divided.

$$A - C \rightleftharpoons B - D$$

$$A + D \rightleftharpoons B + C$$

$$K_4 = \frac{[A][D]}{[B][C]}$$

Here $$K_4 = \frac{K_1}{K_2}$$

(ii) The equilibrium of the backward reaction is the reciprocal of the equilibrium constant of the forward reaction.

$$A + B \rightleftharpoons C + D \quad K = \frac{[C][D]}{[A][B]}$$

$$C + D \rightleftharpoons A + B \quad K' = \frac{[A][B]}{[C][D]}$$

Therefore, $$K' = \frac{1}{K} \tag{9.7}$$

(iii) If a chemical equation is multiplied by a common factor (n), then the new equilibrium constant should also reflect the change. For example,

$$\begin{aligned} A + B &\rightleftharpoons C + D & K &= \frac{[C][D]}{[A][B]} \\ nA + nB &\rightleftharpoons nC + nD & K' &= \frac{[C]^n[D]^n}{[A]^n[B]^n} = (K)^n \end{aligned} \tag{9.8}$$

Note: The relation between reaction type and the equilibrium constant can be summarized as

Reaction	$aA + bB \rightarrow cC + dD$	$cC + dD \rightarrow aA + bB$	$naA + nbB \rightarrow ncC + ndD$
Equilibrium constant	K	$K' = \frac{1}{K}$	$K'' = K^n$

Rules for Writing Equilibrium Constant Expressions

Any reaction that reaches equilibrium, no matter how simple or complex, has an equilibrium constant expression that satisfies the following rules.

1. Even though chemical reactions that reach equilibrium occur in both directions, the substances on the right side of the equation are assumed to be the "products" of the reaction and the substances on the left side of the equation are assumed to be the "reactants".
2. The products of the reaction are always written above the line, in the numerator.
3. The reactants are always written below the line, in the denominator.

4. For systems in which all species are either gases or aqueous solutions, the equilibrium constant expression contains a term for every reactant and every product of the reaction.
5. The numerator of the equilibrium constant expression is the product of the concentrations of each species on the right side of the equation raised to a power equal to the coefficient for that component in the balanced equation for the reaction.
6. The denominator of the equilibrium constant expression is the product of the concentrations of each species on the left side of the equation raised to a power to the coefficient for that component in the balanced equation for the reaction.

Solved Example 9-6

Write the equilibrium constant expression for each of the following reactions.

(a) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

(b) $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$

(c) $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$

(d) $2NO_2(g) \rightleftharpoons N_2O_4(g)$

(e) $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$

Solution

In each case, the equilibrium constant expression is the product of the concentrations of the species on the right side of the equation divided by the product of the concentrations of those on the left side of the equation. All concentrations are raised to the power equal to the coefficient for the species in the balanced equation.

(a) $K = \frac{[NH_3]^2}{[N_2][H_2]^3}$

(b) $K = \frac{[NO]^4[H_2O]^6}{[NH_3]^4[O_2]^5}$

(c) $K = \frac{[PCl_5]}{[PCl_3][Cl_2]}$

(d) $K = \frac{[N_2O_4]}{[NO_2]^2}$

(e) $K = \frac{[SO_2]^2[O_2]}{[SO_3]^2}$

Solved Example 9-7

What is the value of K_C for the following system at equilibrium?

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

At a given temperature, the equilibrium concentrations of the gases are $[NO] = 0.890$ M, $[O_2] = 0.250$ M and $[NO_2] = 0.0320$ M.

Solution

For this reaction, $K = \frac{[NO_2]^2}{[NO]^2[O_2]}$

$$= \frac{[0.0320]^2}{[0.890]^2[0.250]}$$

$$= \frac{1.024 \times 10^{-3}}{0.198} = 5.17 \times 10^{-3}$$

Solved Example 9-8

The rate constant for the following reaction is 1.3×10^4 at 25°C. What happens to the magnitude of the equilibrium constant for a reaction when we turn the equation around?

$$ClNO_2(g) + NO(g) \rightleftharpoons NO_2(g) + ClNO(g)$$

Solution

The magnitude of the equilibrium constant of backward reaction will be inversed.

Solved Example 9-9

The first equilibrium expression (K) as represented by the first chemical equation is 5.81×10^{-7} at 700 K. Calculate the value of the equilibrium expression for the second equation at the same temperature.

$$2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$$
$$SO_3(g) \rightleftharpoons SO_2(g) + \tfrac{1}{2}O_2(g)$$

Solution

The equilibrium expression for $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ is,

$$K = \frac{[SO_2]^2[O_2]}{[SO_3]^2}$$

The equilibrium expression for the second equation, $SO_3(g) \rightleftharpoons SO_2(g) + \frac{1}{2}O_2(g)$ is

$$K = \frac{[SO_2][O_2]^{1/2}}{[SO_3]}$$

Notice the relationship between the two equilibrium expressions

$$\sqrt{\frac{[SO_2]^2[O_2]}{[SO_3]^2}} = \frac{[SO_2][O_2]^{1/2}}{[SO_3]}$$

The equilibrium constant of the second equation is the square root of the first.

$$\sqrt{5.81 \times 10^{-7}} = 7.62 \times 10^{-4}$$

9.4 | HOMOGENEOUS AND HETEROGENEOUS EQUILIBRIA

Chemical equilibrium can be classified into two groups – homogeneous and heterogeneous equilibria. A **homogeneous equilibrium** is established in a system where all reactants and products are in the same phase, such as in a system containing only gases or liquids or solids. Some examples are as follows:

$$2SO_2 + O_2 \rightleftharpoons 2SO_3$$
$$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$$

Equilibria among gases are homogeneous because all gases mix freely with each other, so a single phase exists. There are also many equilibria in which reactants and products are dissolved in the same liquid phase.

A **heterogenous equilibria** is established in a system where the reactants and products are in more than one phase, such as between solid and liquid, liquid and gas, solid and gas, etc.

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$
$$CuO(s) + H_2(g) \rightleftharpoons Cu(s) + H_2O(g)$$

If $NaHCO_3$ is placed in a sealed container so that no CO_2 or H_2O can escape, the gases and solids come to a heterogeneous equilibrium.

$$2NaHCO_3(s) \rightleftharpoons Na_2CO_3(s) + H_2O(g) + CO_2(g)$$

The equilibrium law for this reaction can be written as

$$\frac{[Na_2CO_3(s)]\,[H_2O(g)]\,[CO_2(g)]}{[NaHCO_3(s)]^2} = K$$

However, the equilibrium law for reactions involving pure liquids and solids can be written in an even simpler form. This is because the concentration of a pure liquid or solid is unchangeable at a given temperature. *For any pure liquid or solid, the ratio of amount of substance to volume of substance is a constant.* For example, if we had a 1 mol crystal of $NaHCO_3$, it would occupy a volume of 38.9 cm^3. Two moles of $NaHCO_3$ would occupy twice this volume, 77.8 cm^3, but the *ratio* of moles to liters (i.e., the molar concentration) remains the same.

1 mol $NaHCO_3$

38.9 cm^3

$$\text{Molarity} = \frac{1 \text{ mol } NaHCO_3}{0.0389 \text{ L}}$$
$$= 25.7 \text{ mol L}^{-1}$$

1 mol $NaHCO_3$

77.8 cm^3

$$\text{Molarity} = \frac{2 \text{ mol } NaHCO_3}{0.0778 \text{ L}}$$
$$= 25.7 \text{ mol L}^{-1}$$

Similar reasoning shows that the concentration of Na_2CO_3 in pure solid Na_2CO_3 is a constant, too. This means that the equilibrium law now has three constants, K plus two of the concentration terms. It makes sense to combine all of the numerical constants together.

$$[H_2O(g)][CO_2(g)] = \frac{K[NaHCO_3(s)]^2}{[Na_2CO_3(s)]} = K_C$$

Similarly, for decomposition of calcium carbonate

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

The equilibrium constant of the reaction will be determined only by the equilibrium concentration or pressure of gaseous carbon dioxide.

$$K_C = \frac{[CaO][CO_2]}{[CaCO_3]} = K'[CO_2] \text{ (as concentrations of CaO and } CaCO_3 \text{ are constant)}$$

$$K_p = \frac{p_{CO_2}}{p^o} = p_{CO_2} \quad \text{(at 1 atm pressure)}$$

Note: In heterogeneous equilibrium, it simplifies equations if we replace concentration by activity. In thermodynamics, the activity of pure liquids and solids is taken as unity. So if a reactant or a product is a pure liquid or a solid, we can omit writing it in the equilibrium constant expression.

Solved Example 9-10

When baking soda is heated in a sealed tube, if the equilibrium pressure is 1.04 atm at 398 K, calculate the equilibrium constant for the reaction at 398 K.

Solution

The reactions involved is

$$2NaHCO_3(s) \rightleftharpoons Na_2CO_3(s) + CO_2(g) + H_2O(g)$$

Since, there are only two gaseous species in the above equilibrium, so we have their partial pressures as

$$p_{CO_2} = p_{H_2O} = \frac{p_{\text{total}}}{2} = \frac{1.04}{2} = 0.52 \text{ atm}$$

$$K_p = p_{CO_2} \times p_{H_2O} = [0.52]^2 = 0.2704 \text{ atm}$$

Solved Example 9-11

At a certain temperature, K_p for dissociation of solid $CaCO_3$ is 4×10^{-2} atm and for the second reaction,

$$C(s) + CO_2(g) \rightleftharpoons 2CO(g)$$

is 2.0 atm, respectively. Calculate the partial pressure of CO at this temperature.

Solution

For the reaction $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$,

$$K_p = p_{CO_2} = 4 \times 10^{-2} \text{ atm}$$

In the reaction $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$,

$$K_p = \frac{(p_{CO})^2}{(p_{CO_2})} = 2.0 \text{ atm}$$

Therefore,

$$(p_{CO})^2 = 4 \times 10^{-2} \times 2.0 \Rightarrow p_{CO} = \sqrt{4 \times 10^{-2} \times 2} = 0.28 \text{ atm}$$

Solved Example 9-12

Consider the following heterogeneous equilibrium

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

At 800°C, the pressure of CO_2 is 0.236 atm. Calculate (a) K_p and (b) K_C for the equilibrium reaction at this temperature.

Solution

For the given equilibrium, $K_p = p_{CO_2} = 0.236$ atm. Now, for an equilibrium reaction, $K_p = K_C(RT)^{\Delta n}$. As $\Delta n = 1$, we have

$$K_C = \frac{K_p}{RT} = \frac{0.236}{0.0821 \times 1073} = 2.68 \times 10^{-3} \text{ mol L}^{-1}.$$

Solved Example 9-13

At a certain temperature and total pressure of 10^5 Pa, iodine vapor contains 40% by volume of I atoms:

$$I_2(g) \rightleftharpoons 2I(g)$$

Calculate K_p for the equilibrium.

Solution

Partial pressure of I atoms is

$$p_I = \frac{40}{100} \times p_{total} = \frac{40}{100} \times 10^5 = 4 \times 10^4 \text{ Pa}$$

Partial pressure of I_2 molecules is

$$p_{I_2} = \frac{60}{100} \times p_{total} = \frac{60}{100} \times 10^5 = 6 \times 10^4 \text{ Pa}$$

Now, for the given reaction,

$$K_p = \frac{(p_I)^2}{p_{I_2}} = \frac{(4 \times 10^4)^2 \text{ Pa}^2}{6 \times 10^4 \text{ Pa}} = 2.67 \times 10^4 \text{ Pa}$$

Solved Example 9-14

Calculate the equilibrium constant for the reaction

$$Cu(s) + 2Ag^+(aq) \rightleftharpoons Cu^{2+}(aq) + 2Ag(s)$$

Given that equilibrium concentrations are $[Ag^+] = 1.0 \times 10^{-11}$ mol L^{-1} and $[Cu^{2+}] = 2.0 \times 10^{-7}$ mol L^{-1} at 300 K.

Solution

The reaction represents a heterogeneous equilibrium, so the equilibrium constant will depend only on concentrations of Ag^+ and Cu^{2+} ions, while activity of solid substances is taken as unity. Thus, for the reaction

$$Cu(s) + 2Ag^+(aq) \rightleftharpoons Cu^{2+}(aq) + 2Ag(s)$$

The equilibrium constant expression is

$$K_C = \frac{[Cu^{2+}(aq)][Ag(s)]^2}{[Cu(s)][Ag^+]^2}$$

$$= \frac{2 \times 10^{-7} \text{ mol L}^{-1}}{(1 \times 10^{-11} \text{ mol L}^{-1})^2}$$

$$= 2 \times 10^{15} \text{ mol L}^{-1}$$

Solved Example 9-15

Write the equilibrium law for the following heterogeneous reactions.

(a) $2Hg(l) + Cl_2(g) \rightleftharpoons Hg_2Cl_2(s)$

(b) $Na(s) + H_2O(l) \rightleftharpoons NaOH(aq) + H_2(g)$

(c) Dissolving solid Ag_2CrO_4 in water:

$Ag_2CrO_4(s) \rightleftharpoons 2Ag^+(aq) + CrO_4^{2-}(aq)$

(d) $CaCO_3(s) + H_2O(l) + CO_2(aq) \rightleftharpoons Ca^{2+}(aq) + 2HCO_3^-(aq)$

Solution

(a) $K = \dfrac{1}{[Cl_2]}$

(b) $K = [Na^+][OH^-][H_2]$

(c) $K = [Ag^+]^2[CrO_4^{2-}]$

(d) $K = \dfrac{[Ca^{2+}][HCO_3^-]^2}{[CO_2]}$

9.5 | APPLICATIONS OF EQUILIBRIUM CONSTANTS

The magnitude of an equilibrium constant gives us some idea of the extent to which the reaction proceeds at equilibrium and also its direction. They also help in calculating equilibrium concentrations. Equilibrium calculations for gaseous reactions can be performed using either K_p or K_C, but for reactions in solution we must use K_C. Whether we deal with concentrations or partial pressures, however, the same basic principles apply.

Predicting the Extent of Reaction

Equilibrium constant can be used to compare the extents to which two or more reactions proceed to completion. It is directly proportional to the concentration of products appearing in the numerator of the equilibrium expression and inversely proportional to the concentration of the reactants that appear in the denominator. So, a high value of equilibrium constant implies that the concentration of products is high and vice versa. For example, the reaction

$$2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g)$$

has $K_C = 9.1 \times 10^{80}$ at 25 °C. For an equilibrium between these gases,

$$K_C = \frac{[H_2O]^2}{[H_2]^2[O_2]} = \frac{9.1 \times 10^{80}}{1}$$

By writing K_C as a fraction $(9.1 \times 10^{80})/1$, we see that the numerator of the mass action expression must be large compared to the denominator, which means that the concentration of H_2O is huge compared with the concentrations of H_2 and O_2. At equilibrium, therefore, almost all of the hydrogen and oxygen atoms in the system are found in H_2O molecules and very few are present in H_2 and O_2. Thus, the large value of K_C tells us that the position of equilibrium in this reaction lies far towards the right and that the reaction of H_2 and O_2 goes essentially to completion. The reaction between N_2 and O_2 to give NO:

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

has a very small equilibrium constant; $K_C = 4.8 \times 10^{-31}$ at 25 °C. The equilibrium law for the reaction is

$$\frac{[NO]^2}{[N_2][O_2]} = 4.8 \times 10^{-31} = \frac{4.8}{10^{31}}$$

Here the denominator is very large compared to the numerator, so the concentrations of N_2 and O_2 must be very much larger than the concentration of NO. This means that in a mixture of N_2 and O_2 at this temperature, the amount of NO that is formed is negligible. The reaction hardly proceeds at all towards completion before equilibrium is reached, and the position of equilibrium lies far towards the left.

The decomposition reaction of dinitrogen tetraoxide in gaseous phase

$$N_2O_4 \rightleftharpoons 2NO_2$$

has equilibrium constant $K_C = 4.64 \times 10^{-3}$ at 25°C, which is not very large or small. The equilibrium law for the reaction is

$$\frac{[NO_2]^2}{[N_2O_4]} = 4.64 \times 10^{-3} = \frac{4.64}{10^3}$$

Here the difference between the denominator and the numerator is not too large, so appreciable concentrations of both NO_2 and N_2O_4 exist in the reaction mixture.

The relationship between the equilibrium constant and the position of equilibrium can thus be summarized as follows:

1. When K is very large, that is, $K > 10^3$, the reaction proceeds far towards completion. The position of equilibrium lies far to the right, towards the products.
2. When K is very small, that is, $K < 10^{-3}$, extremely small amounts of products are formed. The position of equilibrium lies far to the left, towards the reactants.

3. When the equilibrium constant lies between 10^{-3} and 10^{3}, the equilibrium mixture contains substantial concentration of both reactants and products. A special case is when $K \approx 1$, then the concentrations of reactants and products are nearly the same at equilibrium. The position of equilibrium lies approximately midway between reactants and products.

Note: Take care in making such comparisons, however, because unless the values of K are greatly different, the comparison is valid only if both reactions have the same number of reactant and product molecules appearing in their balanced chemical equations.

Predicting the Direction of Reaction

We have seen that for any chemical system at equilibrium, the equilibrium constant can be calculated from equilibrium concentrations of reactants and products. For example, the reaction of hydrogen gas with iodine in the gas phase at 440 °C has equilibrium constant of 49.5, when measured experimentally at different equilibrium concentrations. Therefore, for the reaction

$$H_2 + I_2 \rightleftharpoons 2HI$$

$$K_C = \frac{[HI]^2}{[H_2][I_2]}$$

If the reaction has not reached equilibrium, the ratio of concentrations of products and reactants does not give the equilibrium constant, instead

$$\frac{[HI]^2}{[H_2][I_2]} = Q$$

where Q is known as the **reaction quotient**. It can be defined as Q_C for molar concentrations of reactants and products, and as Q_p for partial pressures of gaseous reactants and products. For example, if in the above reaction, the concentrations of H_2, I_2 and HI are measured at any time t, when the reaction may or may not have reached equilibrium as 0.280 mol, 0.145 mol and 0.190 mol, respectively, at 440 °C then

$$\frac{[HI]^2}{[H_2][I_2]} = \frac{(1.90)^2}{(0.280)(0.145)} = 88.91$$

The value of reaction quotient is more than that of equilibrium constant (49.5), so the reaction is not at equilibrium.

Reaction quotient is expressed for any reaction in the same way as for equilibrium constant, except that the concentrations may not necessarily be equilibrium. In general, for a reaction of the type

$$aA + bB \rightleftharpoons cC + dD$$

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{9.9}$$

or in terms of pressure, we have

$$Q = \frac{(p_C)^c(p_D)^d}{(p_A)^a(p_B)^b} \tag{9.10}$$

If concentrations other than equilibrium concentrations are used in the expression, then the comparison of Q_C and K_C values can help predict the direction of reaction (Table 9.1).

Table 9.1 Relation between Q and K values and the direction of reaction

Q and K values	Relative concentration	Direction of net reaction
$Q > K$	Products more than reactants	From right to left
$Q < K$	Reactants more than products	From left to right
$Q = K$	Equilibrium concentrations	No net reaction

Solved Example 9-16

In the formation of nitrosyl chloride from nitric oxide and chlorine by the following reaction

$$2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$$

The equilibrium constant is 6.5×10^4 at 35 °C. The number of moles of NO, Cl_2 and NOCl in the reaction mixture were measured as 0.02 mol, 0.8 mol and 6.8 mol, respectively, in a 2 L flask. In which direction would the reaction proceed at that point in time to attain equilibrium?

Solution

The reaction quotient at any point can be calculated from the molar concentrations of the reactants and products. Given that

$$[NO] = \frac{0.02 \text{ mol}}{2 \text{ L}} = 0.01 \text{ mol L}^{-1}$$

$$[Cl_2] = \frac{0.8 \text{ mol}}{2 \text{ L}} = 0.4 \text{ mol L}^{-1}$$

$$[NOCl] = \frac{6.8 \text{ mol}}{2 \text{ L}} = 3.4 \text{ mol L}^{-1}$$

Using these values in expression for Q_C, we get

$$Q_C = \frac{[3.4 \text{ mol L}^{-1}]^2}{[0.01 \text{ mol L}^{-1}][0.4 \text{ mol L}^{-1}]} = \frac{11.56}{0.04} = 2890$$

The value of reaction quotient is less than that of equilibrium constant, so the reaction would proceed in the forward reaction, that is, towards the formation of more products.

Solved Example 9-17

Which of the following reactions will tend to proceed farthest towards completion?

(a) $H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g) \quad K_C = 1.4 \times 10^{-21}$

(b) $2NO(g) \rightleftharpoons N_2(g) + O_2(g) \quad K_C = 2.1 \times 10^{-30}$

(c) $2BrCl(g) \rightleftharpoons Br_2(g) + Cl_2(\text{in } CCl_4 \text{ solution}) \; K_C = 0.145$

Solution

Reaction (b) will proceed farthest to completion since it has the largest value for K_C.

Solved Example 9-18

Under what conditions will the following reactions go in the forward direction?

$$C(s) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g) + X \text{ kcal}$$

Solution

At low temperature, low pressure, excess of C and excess of H_2O, the reaction will move in the forward reaction.

Solved Example 9-19

A mixture of 1.57 mol of N_2, 1.92 mol of H_2 and 8.13 mol of NH_3 is introduced into a 20 L reaction vessel at 500 K. At this temperature, the equilibrium constant K_C for the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ is 1.7×10^2. Is the reaction mixture at equilibrium? If not, what is the direction of the net reaction?

Solution

The reaction can be represented as

	$N_2(g)$	+	$3H_2(g)$	$\rightleftharpoons$	$2NH_3(g)$
Moles	1.57 mol		1.92 mol		8.13 mol
Concentration	1.57/20		1.92/20		8.13/20

The reaction quotient is

$$Q_C = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(8.13/20 \text{ mol L}^{-1})^2}{1.57/20 \text{ mol L}^{-1} \times (1.92/20 \text{ mol L}^{-1})^3}$$

$$\text{or } Q_C = \frac{(0.406)^2}{(0.078) \times (0.096)^3} \text{L}^2 \text{ mol}^2 = 2.38 \times 10^3 \text{ L}^2 \text{ mol}^2$$

Given that $K_C = 1.7 \times 10^2$. Since the value of Q_C is much higher than the value of the equilibrium constant, the reaction mixture is not at equilibrium. The direction of the net reaction is in the backward direction.

Solved Example 9-20

The value of the equilibrium expression (K_p) as represented by the chemical equation is 5.10. If the reaction quotient for a mixture of these species is found to be 6.74×10^{-9}, would the mixture yield more products, more reactants or is it at or near equilibrium? Assume a reaction quotient within a factor of 10 of the equilibrium constant is at equilibrium.

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

Solution

The reaction quotient is equal to the amount of products present over the amount of reactants present. In this problem the reaction quotient is significantly less than the equilibrium constant. In order for the reaction constant to become closer in value to the equilibrium constant, more products must be created.

$$Q_C = \frac{[CO_2][H_2]}{[CO][H_2O]} \quad \text{where } Q_C \ll K_C$$

Calculating Equilibrium Concentrations

To calculate equilibrium concentrations, the following steps are followed:

1. A balanced equation is written for the reaction. Then a concentration table is written beneath the chemical equation in which the concentrations of the substances involved in the reaction are written as it proceeds towards equilibrium. The table has three rows: initial concentrations (those present in the reaction mixture when it is prepared), changes in concentrations (if the reaction mixture is not at equilibrium when it is prepared, the chemical reaction must occur (either to the left or right) to bring the system to equilibrium and when this happens, the concentrations change) and equilibrium concentrations (are the concentrations of the reactants and products when the system finally reaches equilibrium). The concentrations should have the units of molar concentration (mol L^{-1}).
2. In the table define concentration of one of the terms that reacts and reaches state of equilibrium as x. Then using the stoichiometry of the reaction define the concentration of other reactants and products formed in terms of x. The equilibrium concentrations are substituted into the equilibrium equation and the value of x can be determined. The results can be cross-checked by substituting the value of concentrations into the equilibrium equation.

   Consider the following cases:

   Case 1: In a reaction, let the initial moles of A, B, C and D be l, m, n and p. Let the volume of the container be V and the equilibrium constant of the reaction K_C. Then:

$$\begin{array}{lcccccccc} & aA & + & bB & \rightleftharpoons & cC & + & dD \\ \text{At } t=0, & \frac{l}{V} & & \frac{m}{V} & & \frac{n}{V} & & \frac{p}{V} \\ \text{At } t=t_{eq}, & \frac{l-ax}{V} & & \frac{m-bx}{V} & & \frac{n+cx}{V} & & \frac{p+dx}{V} \end{array}$$

$$K_C = \frac{[C]_{eq}^c [D]_{eq}^d}{[A]_{eq}^a [B]_{eq}^b} = \frac{\left(\frac{n+cx}{V}\right)^c \left(\frac{p+dx}{V}\right)^d}{\left(\frac{l-ax}{V}\right)^a \left(\frac{m-bx}{V}\right)^b}$$

   In the above equation, x is the only variable which can be solved to get the equilibrium concentration of all the species.

> **Note:** In case no information is provided about the initial concentrations of products, assume it to be zero.

   Case 2: In a reaction, let the initial pressures of A, B, C and D be p_1, p_2, p_3 and p_4, respectively. Let the total pressure at equilibrium be p_{Total}. The equilibrium partial pressure of all species and equilibrium constant K_p can be determined as follows.

$$\begin{array}{lcccccccc} & aA & + & bB & \rightleftharpoons & cC & + & dD \\ \text{At } t=0, \text{initial} & p_1 & & p_2 & & p_3 & & p_4 \\ \text{At } t=t_{eq}, \text{partial pressure} & p_1-ax & & p_2-bx & & p_3+cx & & p_4+dx \\ \quad\quad \text{at equilibrium} & & & & & & & \end{array}$$

Then,

$$p_{\text{Total}} = (p_1 - ax) + (p_2 - bx) + (p_3 + cx) + (p_4 + dx)$$

In the above equation, x is the only variable which can be solved to get the partial pressure of all the species at equilibrium and K_p also.

Degree of Dissociation

The degree of dissociation is the fraction that undergoes dissociation in a reaction, and is represented by α. Hence,

$$\alpha = \frac{\text{Moles dissociated}}{\text{Initial moles}}$$

Consider the reaction

$$\begin{array}{lccc} & 2\text{HI} & \rightleftharpoons \text{H}_2 & + \ \text{I}_2 \\ \text{Initial moles} & 1 & 0 & 0 \\ \text{Moles at equilibrium} & 1-\alpha & \alpha/2 & \alpha/2 \end{array}$$

where α represents the degree of dissociation. If we would have started with a moles of HI and the moles of HI dissociated is taken as aα, then the degree of dissociation of HI will not be α but would be α/a.

Note: Consider the following reaction for which the degree of dissociation is to be determined.

$$\begin{array}{lcc} & 2\text{A} & \rightleftharpoons \ \text{A}_2 \\ \text{At } t = 0 & a & 0 \\ \text{At } t = t_{\text{eq}} & a - 2x & x \\ & \| & \| \\ & a(1-\alpha) & a\alpha \end{array}$$

In the above example, students make a common mistake, wherein they simply substitute $x = a\alpha$. However, in the above case

$$\frac{2x}{a} = \alpha \Rightarrow x = \frac{a\alpha}{2}$$

Therefore, correct concentrations at equilibrium are

$$[\text{A}] = a[1-\alpha]$$

$$[\text{A}_2] = \frac{a\alpha}{2}$$

Relation between Vapor Density and Degree of Dissociation and Association

Vapour density of a substance is defined as the mass of a certain volume of substance divided by mass of the same volume of hydrogen. For gaseous reaction for which K_p exists, we can relate vapor density with degree of dissociation.

$$\begin{array}{lcc} & \text{A(g)} & \rightleftharpoons \ n\text{B(g)} \\ \text{Initial moles} & C & 0 \\ \text{Moles at equilibrium} & C(1-\alpha) & nC\alpha \end{array}$$

The total number of moles at equilibrium = $C - C\alpha + nC\alpha = C\,[1 + \alpha(n-1)]$.
For gas at equilibrium, we assume it to be ideal. So, we have

$$pV = nRT = \frac{w}{M}RT \Rightarrow M = \frac{w}{V} \times \frac{RT}{p} = \frac{\rho RT}{p}$$

where ρ is the density of gas, w is the weight and M is the molecular weight. Now, $M = 2 \times$ vapor density. So, we have the expression for vapor density as

$$\text{Vapor density} = \frac{\rho RT}{2p} \tag{9.11}$$

Substituting $p = nRT/V$ in the above equation, we have

$$\text{Vapor density} = \frac{\rho RTV}{2nRT} = \frac{\rho V}{2n} = \frac{w}{2n} \tag{9.12}$$

In a closed vessel, the vapor density will be inversely proportional to the number of moles of the gaseous species as ρ is a constant. Thus, we have

$$\frac{(\text{Vapor density})_{\text{initial}}}{(\text{Vapor density})_{\text{eq}}} = \frac{\text{Total moles at equilibrium}}{\text{Initial moles}} \tag{9.13}$$

Suppose (vapor density)$_{\text{initial}}$ = D and (vapor density)$_{\text{eq}}$ = d, respectively, then for the given equilibrium

$$\frac{D}{d} = \frac{C[1+\alpha(n-1)]}{C} = 1+\alpha(n-1)$$

or

$$\frac{D}{d} - 1 = \alpha(n-1) \Rightarrow \frac{D-d}{d} = \alpha(n-1)$$

or

$$\alpha = \frac{D-d}{(n-1)d} \tag{9.14}$$

In case of association, consider the following reation

$$\begin{array}{lccc} & nA & \rightleftharpoons & A_n \\ \text{Initial moles} & 1 & & 0 \\ \text{Moles at time} = t & (1-\alpha) & & \alpha/n \end{array}$$

where α is the degree of association. The total number of moles = $1-\alpha+\dfrac{\alpha}{n} = 1+\alpha\left(\dfrac{1}{n}-1\right)$

Now, from Eq. (9.13), we have

$$\frac{D}{d} = \frac{C\left[1+\alpha\left(\frac{1}{n}-1\right)\right]}{C} = 1+\alpha\left(\frac{1}{n}-1\right) \quad \frac{D}{d}-1 = \alpha\left(\frac{1}{n}-1\right) \Rightarrow \alpha = \left(\frac{D-d}{d}\right)\left(\frac{n}{1-n}\right)$$

Solved Example 9-21

A mixture containing 8.07 mol of hydrogen and 9.08 mol of iodine was heated at 448°C till equilibrium was attained when 13.38 mol of hydrogen iodide was obtained. Calculate the degree of dissociation of hydrogen iodide at 448°C.

Solution

The reaction of formation of HI is as follows:

$$\begin{array}{cccc} H_2 & + & I_2 & \rightleftharpoons 2HI \\ 8.07 & & 9.08 & 0 \\ 8.07-x & & 9.08-x & 2x \end{array}$$

Therefore, from the above data x can be calculated as

$$2x = 13.38 \Rightarrow x = \frac{13.38}{2} = 6.69$$

The equilibrium constant can be calculated as

$$K'_C = \frac{[HI]^2}{[H_2][I_2]}$$

$$= \frac{(2x)^2}{(9.08-x)(8.07-x)}$$

$$= \frac{(13.38)^2}{(9.08-6.69)\times(8.07-6.69)} = 54.279$$

To calculate the dissociation constant of HI, consider the following reaction

$$\begin{array}{ccc} 2HI & \rightleftharpoons & H_2 + I_2 \\ 1 & & 0 \quad 0 \\ 1-2x & & x \quad x \end{array}$$

From the above data, the dissociation constant is given by

$$K_C = \frac{x\times x}{(1-2x)^2} = \frac{x^2}{(1-2x)^2}$$

But $$K_C = \frac{1}{K'_C} = \frac{1}{54.279} = 0.01842$$

Therefore, x can be calculated as

$$\left(\frac{x}{1-2x}\right)^2 = \frac{1}{54.279} \Rightarrow \frac{x}{1-2x} = \sqrt{\frac{1}{54.279}} = \frac{1}{7.3674}$$

or $$7.3674x = 1-2x$$

Therefore, $$x = \frac{1}{9.3674} = 106.75\times10^{-3}\ \text{mol}$$

$$\alpha = 2x = 2\times106.75\times10^{-3} = 213.5\times10^{-3}$$

or Percentage dissociation = 21.35%

Solved Example 9-22

In the dissociation of HI, 20% of HI is dissociated at equilibrium. Calculate K_p for

$$\text{HI} \rightleftharpoons \tfrac{1}{2}\text{H}_2 + \tfrac{1}{2}\text{I}_2$$

Solution

The reaction can be represented as

$$\begin{array}{lccc} & 2\text{HI} \rightleftharpoons & \text{H}_2 & + \ \text{I}_2 \\ \text{Initial moles} & 1 & 0 & 0 \\ \text{Moles at equilibrium} & 1-\alpha & \alpha/2 & \alpha/2 \end{array}$$

Hence, $\alpha = 0.2$ and $\Delta n = 0$. Therefore, $K_p = K_C$. Now,

$$K_p = K_C = \frac{(\alpha/2V)^{1/2}(\alpha/2V)^{1/2}}{(1-\alpha)/V}$$

$$= \frac{\alpha}{2(1-\alpha)} = \frac{0.2}{2\times0.8} = 0.125$$

For a general reaction $x\text{A(g)} + y\text{B(g)} \rightleftharpoons p\text{C(g)} + q\text{D(g)}$ K_p can also be expressed as

$$K_p = \frac{(n_\text{C})^p_\text{eq}(n_\text{D})^q_\text{eq}}{(n_\text{A})^x_\text{eq}(n_\text{B})^y_\text{eq}}\left(\frac{p_\text{T}}{n_\text{T}}\right)^{\Delta n_\text{g}}_\text{eq}$$

where n_C, n_D, n_A and n_B are the respective moles of A, B, C and D at equilibrium and p_T is the total pressure and n_T are the total gaseous moles at equilibrium.

Solved Example 9-23

K_p for the reaction $\text{N}_2\text{O}_4\text{(g)} \rightleftharpoons 2\text{NO}_2\text{(g)}$ is 640 mm Hg at 775 K. Calculate the percentage dissociation of N_2O_4 at equilibrium pressure of 160 mm Hg. At what pressure, the dissociation will be 50%.

Solution

The reaction can be represented as

$$\begin{array}{lcc} & \text{N}_2\text{O}_4 \rightleftharpoons & 2\text{NO}_2 \\ \text{Initial moles} & 1 & 0 \\ \text{Moles at equilibrium} & 1-\alpha & 2\alpha \end{array}$$

The equilibrium constant can be given by

$$K_p = \frac{(n_{\text{NO}_2})^2}{(n_{\text{N}_2\text{O}_4})}\left(\frac{p_\text{T}}{n_\text{T}}\right)^{\Delta n_\text{g}}$$

But, K_p is given by $$K_p = \frac{4\alpha^2}{1-\alpha}\left(\frac{p_\text{T}}{1+\alpha}\right)^1$$

Substituting $K_p = 640$ and $p_\text{T} = 160$ mm Hg, we get

$$4 = \frac{4\alpha^2}{1-\alpha} \Rightarrow \alpha = 0.707$$

or percentage dissociation = 70.7%.

If $\alpha = 0.5$, then the expression is

$$640 = \frac{4\times(0.5)^2}{0.5}\times\frac{p_\text{T}}{1.5} \Rightarrow p_\text{T} = 480\ \text{mm Hg}$$

Solved Example 9-24

Reaction between nitrogen and oxygen takes place as follows:

$$2\text{N}_2\text{(g)} + \text{O}_2\text{(g)} \rightleftharpoons 2\text{N}_2\text{O(g)}$$

If a mixture of 0.482 mol N_2 and 0.933 mol of O_2 is placed in a reaction vessel of volume 10 L and allowed to form N_2O at a temperature for which $K_C = 2.0\times10^{-37}$, determine the composition of the equilibrium mixture.

Solution

The reaction can be expressed as

	$2N_2(g)\ +$	$O_2(g)\ \rightleftharpoons$	$2N_2O$
Initial moles	0.482	0.933	
Moles at equilibrium	$(0.482-x)$	$(0.933-x/2)$	x
Conc. at equilibrium	$\dfrac{(0.482-x)}{10}$	$\dfrac{(0.933-x/2)}{10}$	$\dfrac{x}{10}$

Then,
$$K_C = \frac{(x/10)^2}{\left(\dfrac{0.482-x}{10}\right)^2 \times \left(\dfrac{9.333-x/2}{10}\right)}$$

or
$$2.0\times10^{-37} = \frac{x\times10}{(0.482-x)^2\times(0.933-x/2)}$$
$$= \frac{10x^2}{(0.482)^2\times0.933}$$

Since x is very small, the terms can be approximated as $0.482 - x \approx x$ and $(0.933 - x/2) \approx 0.933$

$$x = \left(\frac{2.0\times10^{-37}\times(0.482)^2\times0.933}{10}\right)^{1/2}$$
$$= (4.33\times10^{-39})^{1/2} = 6.6\times10^{-20}\ \text{mol}$$

Hence, the equilibrium concentrations are

$$[N_2O] = \frac{6.6\times10^{-20}}{10} = 6.6\times10^{-21}\ \text{mol L}^{-1}$$
$$[N_2] = \frac{(0.482-x)}{10} \approx \frac{0.482}{10} = 0.0482\ \text{mol L}^{-1}$$
$$[O_2] = \left(\frac{0.933-x/2}{10}\right) \approx \frac{0.933}{10} = 0.0933\ \text{mol L}^{-1}$$

Solved Example 9-25

A sample of HI was found to be 22% dissociated when equilibrium was reached. What will be the degree of dissociation if hydrogen is added in the proportion of 1 mol for every mole of HI present originally? Assume temperature and pressure to be constant.

Solution

Give that the percentage dissociation = 22, so degree of dissociation = 0.22. The reaction involved is

	$2HI$	$\rightleftharpoons$	$H_2\ +$	I_2
Initial moles	1		0	0
Moles at equilibrium	$1-\alpha = 0.78$		$\alpha/2 = 0.11$	$\alpha/2 = 0.11$

Therefore,
$$K_C = \frac{[H_2][I_2]}{[HI]^2} = \frac{0.11\times0.11}{(0.78)^2} = 0.0199$$

When 1 mol of hydrogen is added starting with 1 mol of HI, we get

$$K_C = \frac{[H_2][I_2]}{[HI]^2} = \frac{(\alpha/2)\times(\alpha/2+1)}{(1-\alpha)^2} = 0.0199$$

Solving, we get $\alpha = 0.037$. So, the addition of 1 mol of H_2 suppresses the dissociation of HI.

Solved Example 9-26

What will be the degree of dissociation of PCl_5 when 0.1 mol of PCl_5 is placed in a 3 L vessel containing chlorine at 0.5 atm pressure and 250°C? ($K_p = 1.78$)

Solution

The reaction involved is

	$PCl_5 \rightleftharpoons$	$PCl_3\ +$	Cl_2
Initial moles	0.1	0	0
Moles at equilibrium	$0.1-x$	x	x

The partial pressures at equilibrium are as follows:

$$p_{PCl_5} = \frac{(0.1-x)RT}{V} \qquad p_{PCl_3} = \frac{xRT}{V} \qquad p_{Cl_2} = \frac{xRT}{V} + 0.5 \tag{1}$$

The equilibrium constant is given by

$$K_p = \frac{(p_{PCl_3})(p_{Cl_2})}{(p_{PCl_5})} = 1.78$$

Substituting Eq. (1) in the above equation, we get

$$1.78=\frac{\left(\frac{xRT}{V}\right)\left(\frac{xRT}{V}+0.5\right)}{\left(\frac{(0.1-x)RT}{V}\right)}=\frac{x(x\times 0.0821\times 523/3)+0.5x}{0.1-x}$$

Solving we get $14.31x^2+2.28x-0.178=0 \Rightarrow x=0.0574$ mol. Therefore,

$$\alpha=\frac{0.0574}{0.1}=0.574$$

Solved Example 9-27

The reaction $CO(g)+H_2O(g) \rightleftharpoons CO_2(g)+H_2(g)$ has $K_C = 4.06$ at 500 °C. Suppose 0.0600 mol each of CO and H_2O are mixed with 0.100 mol each of CO_2 and H_2 in a 1.00 L reaction vessel. What will be the concentrations of all the substances when the mixture reaches equilibrium at that temperature?

Solution

The equilibrium law for the reaction is

$$K_C=\frac{[CO_2][H_2]}{[CO][H_2O]}$$

Let us use the initial concentrations, shown in the first row of the concentration table below, to determine the initial value of the reaction quotient.

$$Q_{\text{initial}}=\frac{(0.100)\times(0.100)}{(0.100)\times(0.100)}=2.78<K_C$$

As indicated, Q_{initial} is less than K_C, so the system is not at equilibrium. To reach equilibrium, Q must become larger, which requires an increase in the concentrations of CO_2 and H_2 as the reaction proceeds. This means that for CO_2 and H_2, the change must be positive, and for CO and H_2O, the change must be negative. Here is the completed concentration table.

	$CO(g)+H_2O(g) \rightleftharpoons$	$CO_2(g)$ +	$H_2(g)$
Initial concentration (M)	0.0600	0.100	0.100
Change in concentration	$-x$	$+x$	$+x$
Equilibrium concentration	$0.0600-x$	$0.100+x$	$0.100+x$

Substituting equilibrium quantities into expression for the equilibrium law gives us

$$\frac{(0.100+x^2)}{(0.0600-x)^2}=4.06$$

Taking the square root of both sides yields

$$\frac{0.100+x}{0.0600-x}=2.01$$

Solving the equation for x, we get

$$x+2.01x=0.121-0.100$$
$$3.01x=0.021 \Rightarrow x=0.0070\ \text{M}$$

Now we can calculate the equilibrium concentrations:

$$[CO]=[H_2O]=(0.0600-x)=0.0600-0.0070=0.0530\ \text{M}$$
$$[CO_2]=[H_2]=(0.100+x)=0.100+0.0070=0.107\ \text{M}$$

Solved Example 9-28

Ethyl acetate is produced from acetic acid and ethanol by the reaction

$$\underset{\text{Acetic acid}}{CH_3COOH(aq)}+\underset{\text{Ethanol}}{C_2H_5OH(aq)} \rightleftharpoons \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5(aq)}+H_2O(aq)$$

At 25 °C, $K_C = 4.10$ for this reaction. In a reaction mixture, the following equilibrium concentrations were observed: $[CH_3COOH] = 0.210$ M, $[H_2O] = 0.00850$ M, and $[CH_3COOC_2H_5] = 0.910$ M. What was the concentration of C_2H_5OH in the mixture?

Solution

From the reaction, we have

$$K_C=\frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}=\frac{(0.910)(0.00850)}{(0.210)[C_2H_5OH]}=4.10$$

Solving, we get $[C_2H_5OH]=8.98\times10^{-3}$ M.

Solved Example 9-29

For the equilibrium

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Complete the table and compute the value of the equilibrium constant.

Initial Concentrations			Equilibrium Concentrations		
$[H_2]$	$[N_2]$	$[NH_3]$	$[H_2]$	$[N_2]$	$[NH_3]$
0.200	0.200	0	?	?	0.0450

Solution

If 0.0450 mol of NH_3 is formed, calculate the number of moles of N_2 that reacted (per liter).

$$0.0450 \text{ mol } NH_3 \times \frac{1 \text{ mol } N_2}{2 \text{ mol } NH_3}$$

$$= 0.0225 \text{ mol } N_2 \text{ reacted (per liter)}$$

The number of moles of H_2 that reacted is

$$0.0450 \text{ mol } NH_3 \times \frac{3 \text{ mol } H_2}{2 \text{ mol } NH_3}$$

$$= 0.0675 \text{ mol } H_2 \text{ reacted (per liter)}$$

At equilibrium, $[N_2]_{eq} = 0.200 - 0.0225 = 0.178$ M and

$$[H_2]_{eq} = 0.200 - 0.0675 = 0.132 \text{ M.}$$

Solved Example 9-30

In the preceding equilibrium, what is the concentration of NH_3 at equilibrium if the equilibrium concentrations of N_2 and H_2 are 0.22 and 0.14 mol L^{-1}, respectively?

Solution

Given that $[N_2]$ = 0.22 mol L^{-1}, $[H_2]$ = 0.14 mol L^{-1} and K_C = 4.95. Therefore, substituting these values in the following expression

$$K_C = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

we get

$$4.95 = \frac{[NH_3]^2}{(0.22)\times(0.14)^3}$$

or

$$[NH_3]^2 = 2.99\times10^{-3} \Rightarrow [NH_3]$$
$$= 5.5\times10^{-2}$$
$$= 0.055 \text{ mol } L^{-1}$$

Solved Example 9-31

Vapor density of the equilibrium mixture of NO_2 and N_2O_4 is found to be 40 for the equilibrium: $N_2O_4 \rightleftharpoons 2NO_2$. Calculate percentage of NO_2 in the mixture.

Solution

We know that vapor density = (molar mass of mixture of $\frac{NO_2 + N_2O_4}{2}$)

or molar mass of $NO_2 + N_2O_4 = 2 \times$ vapor density $= 80$

If the percentage of NO_2 gas be x, and that of N_2O_4 be $1-x$, then we have

$$x(M_{NO_2} + (1-x)\,M_{N_2O_4}) = 80 \qquad (1)$$

Substituting all values in Eq. (1), we get

$$46x + (1-x)\,92 = 80$$

Solving, we get percentage of NO_2, that is, $x = 26.08\%$

Solved Example 9-32

For the reaction $Ag(CN)_2 \rightleftharpoons Ag^+ + 2CN^-$, the K_C at 25°C is 4 × 10^{-19}. Calculate $[Ag^+]$ in solution which was originally 0.1 M in KCN and 0.03 M in $AgNO_3$.

Solution

The reaction can be represented as

$$2KCN + AgNO_3 \rightleftharpoons Ag(CN)_2^- + KNO_3 + K^+$$

	$2KCN$	$AgNO_3$	$Ag(CN)_2^-$	KNO_3	K^+
Initial moles	0.1	0.03	0	0	0
Moles at equilibrium	(0.1 − 0.06)	0	0.03	0.03	0.03

So, $[Ag(CN)_2^-] = 0.03$ M. Now, from the following reaction, we have

	$Ag(CN)_2^- \rightleftharpoons$	Ag^+	$+2CN^-$
Initial moles	0.03	0	0.04
Moles at equilibrium	$(0.03-\alpha)$	α	$0.04+\alpha$

As K_C is too small and dissociation of $Ag(CN)_2^-$ is very less and thus,

$$0.04+\alpha \approx 0.04 \text{ and } 0.03-\alpha \approx 0.03$$

Now, $[Ag(CN)_2^-] = 0.03$; $[Ag^+] = \alpha$; $[CN^-] = 0.04$

Now, $K_C = \dfrac{[Ag^+][CN^-]^2}{[Ag(CN)_2^-]} = \dfrac{\alpha \times (0.04)^2}{0.03} \Rightarrow \alpha = 7.5 \times 10^{-18}$

Solved Example 9-33

The following equilibrium $PbSO_4 + 2I^-(aq) \rightleftharpoons PbI_2(s) + SO_4^{2-}(aq)$ was followed by measuring the concentration of iodide ion. Initially 250 cm^3 of 0.1 M I^- was taken, and after a long interval of time the equilibrium mixture was titrated against 0.25 M $AgNO_3$ solution. The titre value was 62.0 cm^3. Calculate K_C.

Solution

Initial moles of $I^- = \dfrac{250 \times 0.1}{1000} = 25 \times 10^{-3}$ mol

Moles of I^- at equilibrium $= \dfrac{62.0 \times 0.25}{1000} = 15.5 \times 10^{-3}$ mol

Moles I^- reacted $= (25.0-15.5) \times 10^{-3} = 9.5 \times 10^{-3}$ mol

Moles of SO_4^{2-} at equilibrium $= \dfrac{9.5 \times 10^{-3}}{2} = 4.75 \times 10^{-3}$ mol

Now, concentration at equilibrium is as follows:

$$[I^-]_{eq} = 15.5 \times 10^{-3} \times \frac{1000}{250} = 6.2 \times 10^{-2}\,\text{mol L}^{-1};$$

$$[SO_4^{2-}]_{eq} = 4.75 \times 10^{-3} \times \frac{1000}{250} = 1.9 \times 10^{-2}\,\text{mol L}^{-1}.$$

Therefore, the equilibrium constant is

$$K_C = \frac{[SO_4^{2-}]}{[I^-]} = \frac{1.9 \times 10^{-2}}{(6.2 \times 10^{-2})^2} = 4.43 \text{ mol L}^{-1}$$

Solved Example 9-34

For the reaction $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$, show that degree of dissociation of NH_3 is given as:

$$\alpha = \left[1 + \frac{3\sqrt{3}}{4}\frac{p}{K_p}\right]^{-1/2}$$

where p is equilibrium pressure. If K_p of the above reaction is 78.1 atm at 400°C, calculate K_C.

Solution

The reaction is represented as

	$NH_3(g) \rightleftharpoons$	$\frac{1}{2}N_2(g)+$	$\frac{3}{2}H_2(g)$
Initial moles	1	0	0
Moles at equilibrium	$1-\alpha$	$\alpha/2$	$3\alpha/2$

The total number of moles at equilibrium =
$1 - \alpha + \alpha/2 + 3\alpha/2 = 1 + \alpha$
The partial pressure is

$$p_{NH_3} = \left(\frac{1-\alpha}{1+\alpha}\right)p \quad p_{N_2} = \left(\frac{\alpha}{2(1+\alpha)}\right)p \quad p_{H_2} = \left(\frac{3\alpha}{2(1+\alpha)}\right)p$$

Therefore,
$$K_p = \frac{(p_{N_2})^{1/2}(p_{H_2})^{3/2}}{(p_{NH_3})}$$

$$= \frac{\left[\dfrac{\alpha}{2(1+\alpha)}p\right]^{1/2}\left[\dfrac{3\alpha}{2(1+\alpha)}p\right]^{3/2}}{\left[\dfrac{1-\alpha}{1+\alpha}p\right]}$$

$$= \frac{p\alpha^2\sqrt{27}}{4(1-\alpha^2)}$$

Solving, we get $\alpha = \left[16 + \dfrac{3\sqrt{3}}{4}\dfrac{p}{K_p}\right]^{-1/2}$

We know that $K_p = K_C(RT)^{\Delta n} \Rightarrow 78.1 = K_C(0.0821 \times 673)^1$ or $K_C = 1.413$ mol L^{-1}.

Solved Example 9-35

Bromine monochloride, BrCl, decomposes into bromine and chlorine and reaches the equilibrium

$$2\mathrm{BrCl(g)} \rightleftharpoons \mathrm{Br_2(g)} + \mathrm{Cl_2(g)}$$

For which $K_C = 32$ at 500 K. If initially, pure BrCl is present at a concentration of 3.30×10^3 mol $\mathrm{L^{-1}}$, what is its molar concentration at equilibrium.

Solution

From the reaction stoichiometry

	$2\mathrm{BrCl(g)}$	$\rightleftharpoons$	$\mathrm{Br_2(g)}$ +	$\mathrm{Cl_2(g)}$
Initial moles	2 mol		1 mol	1 mol
Moles at equilibrium	$(3.30\times10^{-3}) - x$		$\frac{x}{2}$	$\frac{x}{2}$

Then,

$$K_C = \frac{[\mathrm{Br_2}][\mathrm{Cl_2}]}{[\mathrm{BrCl}]^2} = \frac{(x/2)\times(x/2)}{(3.30\times10^{-3}-x)^2} = \frac{(x/2)^2}{(3.30\times10^{-3}-x)^2}$$

or

$$(32)^{1/2} = \frac{x}{2(3.30\times10^{-3}-x)}$$

This gives,

$$5.66\times2 = \frac{x}{3.30\times10^{-3}-x}$$

$$11.32 = \frac{x}{3.30\times10^{-3}-x} \Rightarrow x = 3.30\times10^{-3}$$

So, $[\mathrm{BrCl}]_{\mathrm{eq}} = 3.03\times10^{-3}$ mol $\mathrm{L^{-1}}$

9.6 | GIBBS ENERGY CHANGE AND CHEMICAL EQUILIBRIUM

A system in equilibrium represents a state of reversibility where the driving and opposing forces in the process are balanced out. The criteria for equilibrium may be expressed in terms of free energy as follows.

When the concentration of all reactants and products is 1 mol $\mathrm{L^{-1}}$, the Gibbs free energy change is represented by ΔG^{o} which is the standard free energy (IUPAC recommended name is Gibbs energy) change. Note that ΔG^{o} is not necessarily the free energy change at equilibrium.

$$\Delta G^{\mathrm{o}} = \Sigma\Delta G_{\mathrm{f}}^{\mathrm{o}}(\text{products}) - \Sigma\Delta G_{\mathrm{f}}^{\mathrm{o}}(\text{reactants})$$

and

$$\Delta G = \Sigma\Delta G_{\mathrm{f}}(\text{products}) - \Sigma\Delta G_{\mathrm{f}}(\text{reactants})$$

The equilibrium constant is independent of the rate of reaction. However, it can be related to the thermodynamics of the reaction and in particular the change in Gibbs energy. When the value of ΔG for a given change is negative, the change occurs spontaneously. We have also seen that a change is non-spontaneous when ΔG is positive. However, when ΔG is neither positive nor negative, the change is neither spontaneous nor non-spontaneous – the system is in a state of equilibrium. This occurs when ΔG is equal to zero.

The relation between ΔG^{o} and the position of equilibrium can be listed as follows:

1. When ΔG^{o} is positive, the position of equilibrium lies close to the reactants and little reaction occurs by the time equilibrium is reached. The reaction will appear to be non-spontaneous.
2. When ΔG^{o} is negative, the position of equilibrium lies close to the products and a large amount of products will have formed by the time equilibrium is reached. The reaction will appear to be spontaneous.
3. When $\Delta G^{\mathrm{o}} = 0$, the position of equilibrium will lie about midway between reactants and products. Substantial amounts of both reactants and products will be present when equilibrium is reached. The reaction will appear to be spontaneous whether we begin with pure reactants or pure products.

We have seen the qualitative way by which the position of equilibrium in a reaction is determined by the sign and magnitude of ΔG^{o}. We have also seen that the direction in which a reaction proceeds depends on where the system composition stands relative to the minimum on the Gibbs energy curve. Thus, the reaction will proceed spontaneously in the forward direction only if it will lead to a lowering of the Gibbs energy (i.e., if ΔG is negative).

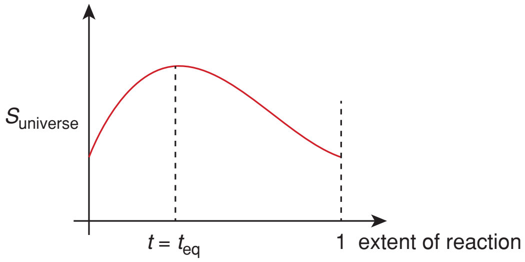


Figure 9.5

where S_{universe} is the total entropy of the universe. Therefore, it can be said that state of equilibrium occurs at maximum value of entropy of universe (Fig. 9.5).

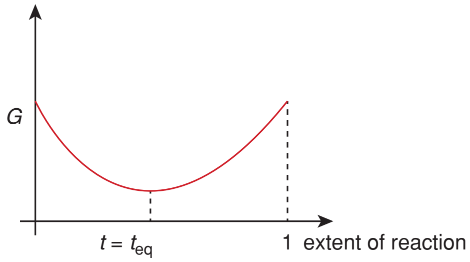


Figure 9.6

Therefore, it can be said that state of equilibrium occurs at minimum value of Gibbs energy (Fig. 9.6).

Note: For a process to be feasible, the entropy of the universe must increase at every point, that is, $\left(\frac{dG}{dn}\right)$ or instantaneous change in Gibbs energy must be negative.

Mathematically, $\left(\frac{dG}{dn}\right) = \left(\frac{dH}{dn}\right) - T\left(\frac{dS}{dn}\right) < 0$

Quantitatively, the relationship between ΔG and ΔG° is expressed by the following equation (which we will not attempt to justify)

$$\Delta G = \Delta G^\circ + RT \ln Q \tag{9.15}$$

where R is the gas constant in appropriate energy units (e.g., $8.314\,\text{J mol}^{-1}\,\text{K}^{-1}$), T is the Kelvin temperature, and $\ln Q$ is the natural logarithm of the reaction quotient. For gaseous reactions, Q is calculated using partial pressures expressed in atm; for reactions in solution, Q is calculated from molar concentrations.

For a reaction in equilibrium, $\Delta G = 0$ and $Q = K_C$, so the Eq. (9.15) reduces to

$$\begin{gathered}\Delta G = \Delta G^\circ + RT \ln K = 0 \\ \Delta G^\circ = -RT \ln K \Rightarrow \ln K = -\frac{\Delta G^\circ}{RT}\end{gathered} \tag{9.16}$$

Taking antilog, we get

$$K = e^{-\Delta G^\circ/RT} \tag{9.17}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Also, $$\Delta G^\circ = -RT \ln K$$

Therefore, $$-RT \ln K = \Delta H^\circ - T\Delta S^\circ$$

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$$

The graph of $\ln K$ vs. $\frac{1}{T}$ is plotted for exothermic and endothermic reaction (Fig. 9.7).

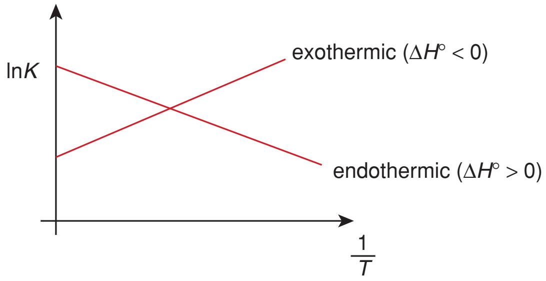


Figure 9.7

Note: Assuming ΔS° and ΔH° to be temperature independent.

$$\ln\frac{K_2}{K_1} = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Equations (9.15) and (9.17) allow us to predict the direction of the spontaneous change in a reaction mixture if we know ΔG° and the composition of the mixture. The results can be summarized as follows:

1. If $\Delta G^\circ < 0$, then $-\Delta G^\circ/RT$ is positive, and therefore, $e^{-\Delta G^\circ/RT} > 1$ or $K > 1$. This implies that the reaction is spontaneous and it proceeds in the forward direction to an extent that products are present predominantly.
2. If $\Delta G^\circ > 0$, then $-\Delta G^\circ/RT$ is negative, and therefore, $e^{-\Delta G^\circ/RT} < 1$ or $K < 1$. This implies that the reaction is non-spontaneous and it proceeds in the forward direction to a small extent, such that very small quantities of products are formed.

Solved Example 9-36

The standard free energy change for a reaction is $\Delta G^\circ = -41.8\,\text{kJ mol}^{-1}$ at 700 K and 1 atm. Calculate the equilibrium constant of the reaction at 700 K.

Solution

The standard free energy and equilibrium constant are related by the equation:

$$\Delta G^\circ = -RT\ln K = -2.303\,RT\log K$$

Given that $\Delta G^\circ = -41.8$ kJ $= -41800$ J, $T = 700$ K and $R = 8.314$ J K^{-1} mol^{-1}. Substituting these values in the equation, we get

$$-41800 = -2.303 \times 8.314 \times 700 \log K$$

$$-41800 = -13403 \log K$$

$$\log K = \frac{41800}{13403} = 3.1187 \Rightarrow K = 1.312 \times 10^4$$

Solved Example 9-37

The reaction $2NO_2(g) \rightleftharpoons N_2O_4(g)$ has $\Delta G^\circ_{298\text{ K}} = -5.40$ kJ mol^{-1} of N_2O_4. In a reaction mixture, the partial pressure of NO_2 is 0.25 atm and the partial pressure of N_2O_4 is 0.60 atm. In which direction must this reaction proceed to reach equilibrium?

Solution

Expressed in terms of partial pressures, the reaction quotient is given by the expression

$$Q_p = \frac{p_{N_2O_4}}{p^2_{NO_2}}$$

Therefore, the equation we will use is

$$\Delta G = \Delta G^\circ + RT\ln\left(\frac{p_{N_2O_4}}{p^2_{NO_2}}\right)$$

Given that:

$\Delta G^\circ_{298\text{ K}} = -5.40$ kJ $\text{mol}^{-1} = -5.40 \times 10^3$ J mol^{-1} = 5.40 kJ $\text{mol}^{-1} = 5.40 \times 10^3$ J mol^{-1}; T = 298 K, $p_{N_2O_4} = 0.60$ atm and $p_{NO_2} = 0.25$ atm, $R = 8.314\,\text{J mol}^{-1}\,\text{K}^{-1}$. Notice we have changed the energy units of ΔG° to joules so they will be compatible with those calculated using R. Substituting the values in the equation, we get

$$\Delta G = -5.40 \times 10^3\ \text{J mol}^{-1} + (8.314\ \text{J mol}^{-1}\ \text{K}^{-1})(298\ \text{K})\ln\left(\frac{0.60}{(0.25)^2}\right)$$

$$= -5.40 \times 10^3\ \text{J mol}^{-1} + (8.314\ \text{J mol}^{-1}\ \text{K}^{-1})(298\ \text{K})\ln(9.6)$$

$$= -5.40 \times 10^3\ \text{J mol}^{-1} + (8.314\ \text{J mol}^{-1}\ \text{K}^{-1})(298\ \text{K}) \times (2.26)$$

$$= -5.40 \times 10^3\ \text{J mol}^{-1} + 5.60 \times 10^3\ \text{J mol}^{-1}$$

$$= +2.0 \times 10^2\ \text{J mol}^{-1}$$

Since ΔG is positive, the forward reaction is non-spontaneous. The reverse reaction is the one that will occur, and to reach equilibrium, some N_2O_4 will have to decompose.

Solved Example 9-38

When 1-pentyne (A) is treated with 4 N alcoholic KOH at 175°C, it is converted slowly into an equilibrium mixture of 1.3% 1-pentyne (A), 95.2% 2-pentyne (B) and 3.5% of 1,2-pentadiene (C).
The equilibrium was maintained at 175°C. Calculate $\Delta G°$ for the following equilibrium:

$$\mathrm{B} \rightleftharpoons \mathrm{A};\quad \Delta G_1^\circ = ?$$
$$\mathrm{B} \rightleftharpoons \mathrm{C};\quad \Delta G_2^\circ = ?$$

From the calculated value of ΔG_1° and ΔG_2° indicate the order of stability of (A), (B) and (C) Write a reasonable reaction mechanism showing all intermediates leading to (A), (B) and (C). **(IIT-JEE 2001)**

Solution

The reaction involved is

$$\underset{\text{(A)}}{\text{1-Pentyne}} + \text{alc.KOH} \rightarrow \underset{\text{(B)}}{\text{2-Pentyne}} + \underset{\text{(C)}}{\text{1,2-Pentadiene}}$$

The equilibrium constant is

$$K_C = \frac{[\mathrm{B}][\mathrm{C}]}{[\mathrm{A}]} = \frac{95.2\times 3.5}{1.3} = 256.31 \qquad (1)$$

Now, from the reaction $\mathrm{B} \rightleftharpoons \mathrm{A}$, $K_1 = [\mathrm{A}]/[\mathrm{B}]$. From the above equation, we have

$$\frac{[\mathrm{C}]}{[\mathrm{A}]/[\mathrm{B}]} = 256.31 \Rightarrow \frac{[\mathrm{C}]}{K_1} = 256.31 \Rightarrow K_1 = \frac{3.5}{256.31} = 0.013$$

The Gibbs energy can be calculated as

$$\Delta G_1^\circ = -2.303RT\log K = -2.303\times 8.314\times 448\ \log 0.013$$
$$= 16178\ \text{J} = 161.178\ \text{kJ}$$

Since ΔG_1° is high, B is more stable than A.
Now, from the second reaction $\mathrm{B} \rightleftharpoons \mathrm{C}$, $K_2 = [\mathrm{C}]/[\mathrm{B}]$. Multiplying and dividing throughout Eq. (1) by $[\mathrm{B}]^2$, we have

$$256.31 = \frac{[\mathrm{C}]/[\mathrm{B}]}{[\mathrm{A}]/[\mathrm{B}]^2} \Rightarrow 256.31 = \frac{K_2}{[\mathrm{A}]/[\mathrm{B}]^2}$$

or $$K_2 = 256.31\times\frac{1.3}{(95.2)^2} = 0.037$$

The Gibbs energy can be calculated as

$$\Delta G_2^\circ = -2.303RT\log K = -2.303\times 8.314\times 448\ \log 0.037$$
$$= 12282\ \text{J} = 12.282\ \text{kJ}$$

Since ΔG_1° is low, B is more stable than C. Thus, the overall order of stability order is B > C > A.

Solved Example 9-39

In the following equilibrium $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, when 5 mol of each are taken, the temperature is kept at 298 K the total pressure was found to be 20 bar. Given that $\Delta G_f^\circ(N_2O_4) = 100$ kJ and $\Delta G_f^\circ(NO_2) = 50$ kJ

(a) Find ΔG of the reaction

(b) The direction of the reaction in which the equilibrium shifts. **(IIT-JEE 2004)**

Solution

(a) For the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, the reaction quotient is

$$Q_p = \frac{p^2_{NO_2}}{p_{N_2O_4}} = \frac{100}{10} = 10\ \text{atm}$$

$$\Delta G^\circ\text{reaction} = 2\Delta G_f^\circ(NO_2) - \Delta G_f^\circ(N_2O_4) \Rightarrow 0$$
$$= 100 - 100$$

$$\Delta G = \Delta G^\circ + RT\ln K$$

$$\text{Therefore}, \Delta G = RT\ln Q_p = 2.303\times 0.082\times 298\times\log 9.9$$
$$= 56.0304\ \text{L atm} = \text{Positive quantity}$$

(b) Therefore, the reaction will shift towards reverse direction.

9.7 | SIMULTANEOUS EQUILIBRIUM

A simultaneous equilibrium occurs when more than one equilibrium exists in the same container simultaneously. In this case, the same species may be involved in more than one equilibrium and its concentration at equilibrium is the same in all those equilibria under the same thermodynamic conditions. For example,

$$\mathrm{CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)}$$
$$\mathrm{CO_2(g) + C(s) \rightleftharpoons 2CO(g)}$$

Hence, $CO_2(g)$ is the common species in both these equilibria and its concentration at equilibrium will be the same for both finally.

Consider the following reactions at simultaneous equilibrium:

$$\begin{array}{lcccccl} & \mathrm{A} & \rightleftharpoons & \mathrm{B} & + & \mathrm{C} & (\text{Equilibrium constant } K_1) \\ \text{At } t=0 & C_1 & & C_2 & & 0 & \\ \text{At } t=t_{\text{eq}} & C_1-x+z & & C_2+x-y+z & & x & \end{array}$$

$$\begin{array}{lcccccl} & \mathrm{B} & \rightleftharpoons & \mathrm{D} & + & \mathrm{E} & (\text{Equilibrium constant } K_2) \\ \text{At } t=0 & C_2 & & 0 & & C_3 & \\ \text{At } t=t_{\text{eq}} & C_2-y+x+z & & y & & C_3+y-z & \end{array}$$

$$\begin{array}{lcccccl} & \mathrm{E} & \rightleftharpoons & \mathrm{B} & + & \mathrm{A} & (\text{Equilibrium constant } K_3) \\ \text{At } t=0 & C_3 & & C_2 & & \mathrm{C}_1 & \\ \text{At } t=t_{\text{eq}} & C_3-z+y & & C_2+z+x-y & & C_1+z-x & \end{array}$$

Given that the initial concentration of A, B, E is C_1, C_2, C_3. Now, A, B and E are the common ions in the simultaneous equilibrium, therefore, their equilibrium concentration must be equal. Therefore,

$$K_1 = \frac{(C_2+x-y+z)(x)}{(C_1-x+z)}$$
$$K_2 = \frac{(C_3+y-z)(y)}{(C_2-y+x+z)}$$
$$K_3 = \frac{(C_2+x-y+z)(C_1+z-x)}{(C_3-z+y)}$$

9.8 | LE CHATELIER'S PRINCIPLE AND FACTORS AFFECTING EQUILIBRIA

Le Chatelier's principle tells us how a chemical equilibrium responds when disturbed. In previous sections, you have seen that it is possible to perform calculations that tell us what the composition of an equilibrium system is. However, many times we really do not need to know exactly what the equilibrium concentrations are. Instead, we may want to know what actions we should take to control the relative amounts of the reactants or products at equilibrium. For instance, if we were preparing ammonia, NH_3, by the reaction of N_2 with H_2, we might want to know how to maximize the yield of NH_3.

Le Chatelier's principle provides us with the means for making qualitative predictions about changes in chemical equilibria. Recall that **Le Chatelier's principle** states that *if an outside influence upsets an equilibrium, the system undergoes a change in a direction that counteracts the disturbing influence and, if possible, returns the system to equilibrium.* Let us examine the kinds of "outside influences" that affect chemical equilibria.

Effect of Change in Concentration

In accordance with Le Chatelier's principle, when the concentration of any of reactants or products in a reaction at equilibrium is changed, the composition of the equilibrium mixture changes so as to minimize the effect of the change. So when the concentration of a reactant is increased or that of a product is decreased, the equilibrium shifts towards the forward direction. Similarly, a decrease in the concentration of any reactant shifts the equilibrium in the reverse direction.

In the reaction of ammonia formation, when additional amount of N_2 is added to the system initially at equilibrium, the system relieves the stress by removal of some of the additional N_2 to form more product ammonia. When the product is removed, the value of Q_C is less than the value of K_C and the reaction moves in the forward direction. An increase in the concentration of a reactant or product ultimately leads to an increase in the concentration of the species on the other side of the equation. Conversely, a decrease in the concentration of a reactant or product ultimately leads to formation of more of that reactant or product.

Note: In reactions where a precipitate forms or a gas is evolved, that product is, in effect, entirely removed from the system. The system shifts to replace this loss, but if the loss is complete, the reaction continues to completion. This is known as an *irreversible reaction*, since products cannot reform reactants.

Consider the example of formation of methane from water gas

$$\mathrm{CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)}$$

If the water vapor is removed from the reaction mixture, according to Le Chatelier's principle, the system shifts in the direction to reinstate the amount of water vapor removed, till the equilibrium is re-established. In other words, the reaction will increase in the forward direction and lead to an effective increase in yield of methane.

Let us consider an experiment to demonstrate the effect of change of concentration on the equilibrium. Iron thiocyanate gives a red colored solution when dissolved in water, due to the presence of hydrated $FeSCN^{2+}$ ions. An equilibrium exists between undissociated $FeSCN^{2+}$ ions and dissociated ferric and thiocyanate ions.

$$\underset{\text{Red}}{\mathrm{(FeSCN)^{2+}(aq)}} \rightleftharpoons \underset{\text{Pale yellow}}{\mathrm{Fe^{3+}(aq)}} + \underset{\text{Colorless}}{\mathrm{SCN^-(aq)}}$$

The following experimental observations were made:

1. On addition of sodium thiocyanate solution, the red color of the solution deepens.
2. On addition of oxalic acid to the solution, the red solution turns yellow.
3. Addition of aqueous $HgCl_2$ decreases the red color of the solution.

These observations can be explained as follows:

1. Addition of NaSCN in the solution increases the concentration of SCN^- ions. The system compensates this addition by shifting the equilibrium towards formation of more iron thiocyanate, which is red in color.
2. When oxalic acid is added to the solution, it binds with the Fe^{3+} ions to form a stable complex of iron oxalate $[Fe(C_2O_4)_3]^{3-}$, thus effectively decreasing the concentration of Fe^{3+} ions. The system compensates for this stress by shifting the equilibrium towards production of more ferric ions, which are yellow in color.
3. When $HgCl_2$ is added to the solution, the Hg^{2+} ions form stable complex ion $[Hg(SCN)_4]^{2-}$ with dissociated SCN^- ions. This shifts the equilibrium of the system in the direction that replenishes the SCN^- ions. The amount of hydrated $FeSCN^{2+}$ is reduced and hence the red color fades.

The experiment thus demonstrates how the system deals with concentration stress on removal or addition of ions into the equilibrium mixture.

Effect of Change in Pressure

Increasing the pressure on a gaseous mixture of reactants and products at equilibrium (or decreasing the volume of the container) is another example of stress on a system. The system can counteract the stress of increased pressure by shifting to a lower volume if possible. In case of gaseous reactions, an increase in pressure shifts the equilibrium in the direction where the number of moles decreases. For example, in the formation of ammonia by Haber process,

$$\mathrm{N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + 92\ kJ}$$

There are four moles of gaseous reactants ($N_2 + 3H_2$) but only two moles of the gaseous product ($2NH_3$). Therefore, the increase in pressure shifts the equilibrium in the forward reaction. In general, an increase in pressure on a gaseous system shifts the point of equilibrium in the direction of the smaller number of moles of gas. Alternately, if there is the same number of moles of gas on each side of the equation, a change in pressure does not shift the point of equilibrium. When gases are not involved in a reaction at equilibrium, such as one in aqueous solution, pressure changes have negligible effect, since solids and liquids are essentially incompressible.

The effect of pressure change on the equilibrium can be understood in terms of how it affects the concentration of gaseous reactants and the products. From the ideal gas equation, we have

$$pV = nRT \Rightarrow p = \frac{n}{V}RT$$

The pressure and volume are inversely related and the concentration term (n/V) is directly related to the pressure of the gas.

We have $p \propto n$. So if we increase pressure, the reaction will go in the direction where number of moles are less and vice versa. For example, consider, the reaction

$$\mathrm{A(g)} \rightleftharpoons \mathrm{2B(g)}$$

Here, $\Delta n_g > 0$. So,

(i) If pressure increases, then n increases, therefore, the reaction will move in the direction where n decreases, that is in the backward direction.

(ii) If pressure decreases, then n decreases, therefore, the reaction will move in the direction where n increases, that is in the forward direction.

Now consider the reaction

$$\mathrm{2A(g)} \rightleftharpoons \mathrm{B(g)}$$

Here, $\Delta n_g < 0$. So,

(i) If pressure increases, then n increases, therefore, the reaction will move in the direction where n decreases, that is in the forward direction.

(ii) If pressure decreases, then n decreases, therefore, the reaction will move in the direction where n increases, that is in the backward direction.

In the following reaction

$$\mathrm{A(g)} \rightleftharpoons \mathrm{B(g)}$$

Here, $\Delta n_g = 0$. So, no effect of change in pressure on the equilibrium is observed.

Consider another example of equilibrium in gaseous phase

$$\mathrm{N_2O_4(g)} \rightleftharpoons \mathrm{2NO_2(g)}$$

The reaction quotient is
$$Q = \frac{[\mathrm{NO_2}]^2}{[\mathrm{N_2O_4}]}$$

When the pressure is increased in the cylinder containing the equilibrium mixture using a movable piston, the volume decreases and the concentration of both NO_2 and N_2O_4 increases. In the expression for reaction quotient, the concentration term for NO_2 is squared, so the numerator increases more than the denominator and the equilibrium state will compensate for the stress by shifting the reaction in the backward direction.

Effect of Change of Volume

We know that $V \propto 1/p$ and $p \propto n$. Therefore, if we increase the volume, the pressure is decreases and the reaction will go in the direction in which the number of moles is more. For example, consider the following reaction:

$$\mathrm{A(g)} \rightleftharpoons \mathrm{2B(g)}$$

Here, $\Delta n_g > 0$. So,

(i) If volume increases, pressure decreases and n decreases, therefore, the reaction will move in the direction where n increases, that is in the forward direction.

(ii) If volume decreases, pressure increases and n increases, therefore, the reaction will move in the direction where n decreases, that is in the backward direction.

Now consider the reaction

$$2A(g) \rightleftharpoons B(g)$$

Here, $\Delta n_g < 0$. So,

(i) If volume increases, then pressure decreases and n decreases, therefore, the reaction will move in the direction where n increases, that is in the backward direction.

(ii) If volume decreases, then pressure increases and n increases, therefore, the reaction will move in the direction where n decreases, that is in the forward direction.

Now consider the following reaction

$$A(g) \rightleftharpoons B(g)$$

Here, $\Delta n_g = 0$. So, no effect of change in volume on the equilibrium is observed.

Effect of Change in Temperature

An increase in temperature favors the forward reaction in the case of an endothermic process and the backward reaction in an exothermic process. For example, in formation of ammonia (exothermic process) low temperature favors the forward reaction and high temperature favors the backward reaction. The equation showing heat as a product can be written as follows.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + 92 \text{ kJ}$$

If we add heat (increase the temperature), the reaction shifts in a direction to remove that heat. If we remove heat by cooling the reaction mixture, the equilibrium shifts in a direction to replace that heat loss. For an exothermic reaction, cooling the reaction mixture increases the concentration of products when equilibrium is re-established. For an endothermic reaction, where heat can be considered as a reactant, heating the reaction mixture increases the concentration of products at equilibrium. An increased concentration of NH_3 at equilibrium is favored at low temperatures. The system attempts to compensate for the loss of heat by formation of more NH_3 and, with it, more heat.

$$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g); \quad \Delta H^\circ = -46.19 \text{ kJ}$$

The equilibrium constant is

$$K_C = \frac{[NH_3]^2}{[H_2]^3[N_2]}$$

or

$$\log \frac{K_{p_2}}{K_{p_1}} = \frac{\Delta H}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \tag{9.18}$$

Similarly, for manufacture of sulphuric acid by contact process, low temperature will also shift the equilibrium in the forward reaction.

$$2SO_2 + O_2 \rightleftharpoons SO_3 + 188.56 \text{ kJ}$$

Note: In the contact process, the forward reaction and hence the yield of sulphur trioxide is also favored by increase in concentration of SO_2 and O_2 and high pressure.

For an exothermic reaction

$$A \rightleftharpoons B + \text{heat}$$

(i) If temperature T increases, the reaction moves in the direction where less heat is evolved, that is, in the backward direction.

(ii) If temperature T decreases, the reaction moves in the direction where more heat is evolved, that is, in the forward direction.

For an endothermic reaction

$$A + \text{heat} \rightleftharpoons B$$

(i) If temperature T decreases, the reaction moves in the direction where less heat is evolved, that is, in the forward direction.

(ii) If temperature T decreases, the reaction moves in the direction where more heat is evolved, that is, in the backward direction.

Effect of Addition of Inert Gas

When an inert gas, such as argon, helium or neon is added to a reaction mixture in equilibrium, the effect on equilibrium constant is determined by the conditions under which the addition is carried out.

1. **Constant volume:** If the inert gas is added such that volume of reaction mixture remains constant, then p_{total} must increase. Initially, $p_{\text{total}} = p_{\text{reactant}} + p_{\text{product}}$ and after addition of inert gas it is $p_{\text{total}} = p_{\text{reactant}} + p_{\text{product}} + p_{\text{inert gas}}$. However, the partial pressures of reactants and products or the concentrations of the products and reactants (i.e., ratio of their moles to the volume of the container) are not changed. So, there is no shift in the equilibrium.
2. **Constant pressure:** If the inert gas is added such that the pressure of equilibrium mixture does not change, then the total volume of the gases must increase. Here, initially, $p_{\text{total}} = p_{\text{reactant}} + p_{\text{product}}$ and after addition of inert gas it is $p_{\text{total}} = p_{\text{reactant}} + p_{\text{product}} + p_{\text{inert gas}}$. Since, p_{total} before and after addition of inert gas is the same, so partial pressures of the reactants and products must undergo a change. In other words, the number of moles per unit volume of various reactants and products will decrease. Hence, the equilibrium will shift towards the direction in which there is increase in number of moles of gases.

For example, if helium is added in the reaction of decomposition of dinitrogen tetraoxide at constant volume, the total pressure of the gases increases and the mole fraction of NO_2 and N_2O_4 decreases. However, since the partial pressures of each gas do not change as the product of mole fraction and total pressure remain the same, the equilibrium is not affected.

Some Special Cases

In case of equilibrium in which activity of reactant and product is unity, in some cases on increasing pressure, the reaction goes in the direction where volume decreases. For example,

$$\underset{\text{(graphite)}}{\text{Carbon}} \rightleftharpoons \underset{\text{(diamond)}}{\text{Carbon}} \qquad \Delta H = \text{positive}$$

Here, as density (d) increases, volume (V) decreases (in going from graphite to diamond) and vice versa. Therefore, on increase in pressure, the reaction goes in the direction where the volume is less, that is, in the forward direction. Similarly, on increase in temperature, the reaction goes in the forward direction. Thus formation of diamond from graphite is favorable at high pressure and temperature.
Now consider the case of conversion of ice into water.

$$\underset{\text{(ice)}}{H_2O} \rightleftharpoons \underset{\text{(water)}}{H_2O} \qquad \Delta H = \text{positive}$$

Usually on the density of substance as solid is more than its density in the liquid form. However, ice is an exception to this property. So the density decreases and volume increases as ice is converted to water and vice versa for conversion of water into ice. Therefore, on increase in pressure, the reaction goes in the direction where volume is less, that is, in the forward direction. On increasing temperature, the reaction moves in the forward direction. Thus melting of ice is favored at high temperature and high pressure.

Effect of Adding Catalyst

Fritz Haber discovered a heterogeneous catalyst (certain transition metal oxides) that increased the rate of synthesis of ammonia. In the presence of the catalyst, the reaction can be run at around 500°C instead of over 1000°C without a catalyst. At the lower temperature, the reaction proceeds smoothly with a significant yield of NH_3.

A catalyst in a system that reaches a point of equilibrium increases the rate of both the forward and reverse reactions proportionally, but does not change the point of equilibrium. The function of a catalyst is simply to reach the point of equilibrium in less time. If K of a reaction has a very small value, a catalyst cannot play a major role. However, with a catalyst, exothermic reactions can be run at considerably lower temperatures, thus increasing the yield of products.

The use of catalyst can also influence the formation of one of the products in preference, when the possibility of formation of more than one products exists in the equilibrium reaction mixture. This is illustrated in the case of Ostwald process for the synthesis of nitric acid. The nitric oxide used is prepared by oxidation of ammonia.

$$4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$$

The nitric oxide formed then undergoes the following reactions to form nitric acid:

$$2NO(g) + 5O_2(g) \rightarrow 2NO_2(g)$$
$$3NO_2(g) + H_2O(l) \rightarrow 2HNO_3(aq)$$

or it may dissociate to its elements

$$2NO(g) \rightleftharpoons N_2(g) + O_2(g)$$

The equilibrium mixture may thus contain dinitrogen and water instead of nitric oxide

$$4NH_3(g) + 3O_2(g) \rightleftharpoons 2N_2(g) + 6H_2O(g)$$

It was discovered by German chemist Wilhelm Ostwald that the use of platinum catalyzed the reaction of oxidation of ammonia to nitric oxide. Using this catalyst, nitric oxide can be obtained at moderate temperatures under which its dissociation into the elements (N_2 and O_2) does not take place.

Solved Example 9-40

For the formation of ammonia the equilibrium constant data at 673 K and 773 K, respectively, are 1.64×10^{-4} and 1.44×10^{-5}, respectively. Calculate heat of the reaction. Given $R = 8.314\,\text{J K}^{-1}\,\text{mol}^{-1}$.

Solution

Substituting the values in the equation

$$\ln \frac{K_{p_2}}{K_{p_1}} = \frac{\Delta H}{R}\left[\frac{T_2 - T_1}{T_2 T_1}\right]$$

we get

$$2.303 \log \frac{1.44 \times 10^{-5}}{1.64 \times 10^{-4}} = \frac{\Delta H}{8.314}\left[\frac{773 - 673}{773 \times 673}\right]$$

$$2.303 \log(0.0878) = \frac{\Delta H(100)}{8.314 \times 773 \times 673}$$

or $100 \times \Delta H = 2.303 \times (-1.0565) \times 673 \times 773 \times 8.314$

hence
$$\Delta H = \frac{673 \times 773 \times 2.303 \times -1.0565 \times 8.314}{100}$$
$$= -105216\ \text{J} = -105.216\ \text{kJ}$$

Solved Example 9-41

The reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ is endothermic, with $\Delta H° = +56.9$ kJ. How will the amount of NO_2 at equilibrium be affected by **(a)** adding N_2O_4, **(b)** lowering the pressure by increasing the volume of the container, **(c)** raising the temperature, and **(d)** adding a catalyst to the system? Which of these changes will alter the value of K_C?

Solution

We are applying various types of disturbances to an equilibrium mixture of NO_2 and N_2O_4. The tool we use to judge the effects of such disturbances is Le Chatelier's principle. As we discussed above, we expect the equilibrium to shift to the left or right to counteract the disturbance in most cases.

(a) Adding N_2O_4 will cause the equilibrium to shift to the right, that is, in a direction that will consume some of the added N_2O_4. The amount of NO_2 will increase.

(b) When the pressure in the system drops, the system responds by producing more molecules of gas, which will tend to raise the pressure and partially offset the change. Since more gas molecules are formed if some N_2O_4 decomposes, the amount of NO_2 at equilibrium will increase.

(c) Because the reaction is endothermic, we write the equation showing heat as a reactant:

$$\text{Heat} + N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

Raising the temperature is accomplished by adding heat, so the system will respond by absorbing heat. This means that the equilibrium will shift to the right and the amount of NO_2 at equilibrium will increase.

(d) A catalyst causes a reaction to reach equilibrium more quickly, but it has no effect on the position of chemical equilibrium. Therefore, the amount of NO_2 at equilibrium will not be affected.

Finally, the *only* change that alters K is the temperature change. Raising the temperature (adding heat) will increase K_C for this endothermic reaction.

Solved Example 9-42

Consider the equilibrium $PCl_5(g) + 4H_2O(g) \rightleftharpoons H_3PO_4\ (l) + 5HCl(g)$. How will the amount of H_3PO_4 at equilibrium be affected by decreasing the volume of the container holding the reaction mixture?

Solution

This is an example of heterogeneous equilibrium. Only the gases will be affected by the volume of the container. But the stoichiometric ratio of the reactants to products is 5:5, so as the volume is changes, the number of moles of gas will not change, therefore the reaction will not change, and there will be no change in the amount of H_3PO_4.

Solved Example 9-43

Consider the equilibrium $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$, for which $\Delta H° = -88\,kJ$. How will the amount of Cl_2 at equilibrium be affected by **(a)** adding PCl_3, **(b)** adding PCl_5, **(c)** raising the temperature, and **(d)** decreasing the volume of the container? How (if at all) will each of these changes affect K_p for the reaction?

Solution

(a) The equilibrium will shift to the right, decreasing the concentration of Cl_2 at equilibrium, and consuming some of the added PCl_3. The value of K_p will be unchanged.

(b) The equilibrium will shift to the left, consuming some of the added PCl_5 and increasing the amount of Cl_2 at equilibrium. The value of K_p will be unchanged.

(c) For any exothermic equilibrium, an increase in temperature causes the equilibrium to shift to the left, in order to remove energy in response to the stress. This equilibrium is shifted to the left, making more Cl_2 and more PCl_3 at the new equilibrium. The value of K_p is given by the following:

$$K_p = \frac{p_{PCl_5}}{p_{PCl_3} \times p_{Cl_2}}$$

In this system, an increase in temperature (which causes an increase in the equilibrium concentrations of both PCl_3 and Cl_2 and a decrease in the equilibrium concentration of PCl_5) causes an increase in the denominator of the above expression as well as a decrease in the numerator of the above expression. Both of these changes serve to decrease the value of K_p.

(d) Decreasing the container volume for a gaseous system will produce an increase in partial pressures for all gaseous reactants and products. In order to lower the increase in partial pressures, the equilibrium will shift so as to favor the product side having the smaller number of gaseous molecules, in this case to the right. This shift will decrease the amount of Cl_2 and PCl_3 at equilibrium, and it will increase the amount of PCl_5 at equilibrium. While the change in volume will change the position of the equilibrium, it does not change the value for K_p.

Solved Example 9-44

When 3.06 g of solid NH_4HS is introduced into a 2 L evacuated flask at 270°C, 30% of the solid decomposes into gaseous ammonia and hydrogen sulphide

(a) Calculate K_C and K_p for the reaction at 27°C.

(b) What would happen to equilibrium when more solid NH_4HS is introduced into the flask? **(IIT-JEE 1999)**

Solution

The reaction along with the given data is

	$NH_4HS(s)$	$\rightleftharpoons$	$NH_3(g)$	+	$H_2S(g)$
Initial moles	3.06 g = –0.06 mol		0		0
Moles at equilibrium	0.7×0.06 mol		0.3×0.06 mol		0.3×0.06 mol

(a) The equilibrium constant K_C is

$$K_C = [NH_3(g)][H_2S(g)] = \left(\frac{0.018}{2}\right)\left(\frac{0.018}{2}\right)$$
$$= 8.1 \times 10^{-5}\ mol^2\ L^{-2}$$

The equilibrium constant K_p is

$$K_p = K_C(RT)^{\Delta n} = (8.1 \times 10^{-5})[0.082 \times 300]^2$$
$$= 4.90 \times 10^{-2}\ atm^2$$

(b) No effect on the equilibrium will be observed by introducing more of solid NH_4HS as the equilibrium constant does not depend of the concentration of solid NH_4HS.

Solved Example 9-45

The equilibrium constant for the reaction $H_2 + I_2 \rightleftharpoons 2HI$ is found to be 64 at 450°C. If 6 mol of hydrogen are mixed with 3 mol of iodine in a liter vessel at this temperature, what will be the concentration of each of the three components, when equilibrium is attained? If the volume of reaction vessel is reduced to half, then what will be the effect on equilibrium?

Solution

The equilibrium reaction can be represented as:

	H_2	+	I_2	$\rightleftharpoons$	$2HI$
Initial moles	6		3		0
Moles at equilibrium	$6-x$		$3-x$		$2x$
Concentration at equilibrium	$\frac{6-x}{1}$		$\frac{3-x}{1}$		$\frac{2x}{1}$

The equilibrium constant is

$$K_C = \frac{(2x)^2}{(6-x)(3-x)} \Rightarrow 64 = \frac{4x^2}{x^2+18-9x}$$

$$16(x^2 - 9x + 18) = x^2$$

Solving, we get $x = 2.84$. Hence, the concentration of the species at equilibrium is

$$[HI] = \frac{2x}{1} = \frac{2\times 2.84}{1} = 5.68\,M$$

$$[H_2] = \frac{6-x}{1} = \frac{6-2.84}{1} = 3.16\,M$$

$$[I_2] = \frac{3-x}{1} = \frac{3-2.84}{1} = 0.16\,M$$

In the present reaction, $\Delta n = 0$; hence, volume change will not affect the equilibrium.

Solved Example 9-46

The reaction $CuSO_4 \cdot 3H_2O(s) \rightleftharpoons CuSO_4 \cdot H_2O(s)$ has the dissociation pressure is 7×10^{-3} atm at 25°C and $\Delta H° = 2750$ cal. What will be the dissociation pressure at 127°C?

Solution

The equilibrium constant is $K_p = (p_{H_2O})^2 = (7\times 10^{-3})^2\ \text{atm}^2 = 4.9\times 10^{-5}\ \text{atm}^2$

Since $\Delta H° = 2750$ cal, so using van't Hoff equation, we get

$$\log\frac{[K_p(127°C)]}{[K_p(25°C)]} = \frac{\Delta H°}{2.303\times R}\left[\frac{400-298}{400\times 298}\right]$$

or

$$\log\frac{[K_p(127°C)]}{[4.9\times 10^{-5}]} = \frac{2750}{2.303\times 2}\left[\frac{102}{119200}\right]$$

On solving, we get $K_p(127°C) = 3.2426 \times 4.9 \times 10^{-5}$ so

$$p_{H_2O}(127°C) = \sqrt{K_p(127°C)} = 1.26\times 10^{-2}\ \text{atm}$$

Solved Example 9-47

Describe the effect of **(a)** addition of H_2, **(b)** addition of CH_3OH, **(c)** removal of CO and **(d)** removal of CH_3OH on the equilibrium of the reaction:

$$2H_2(g) + CO(g) \rightleftharpoons CH_3OH(g)$$

Solution

The equilibrium constant for the given reaction is

$$K_C = \frac{[CH_3OH]}{[H_2]^2[CO]}$$

(a) Addition of H_2 will shift the reaction in the forward direction.

(b) Addition of CH_3OH will shift the reaction in the reverse direction.

(c) When CO is removed, the reaction will move in the reverse direction.

(d) When CH_3OH is removed, the reaction will move in the forward direction.

SOLVED OBJECTIVE QUESTIONS FROM PREVIOUS YEAR PAPERS

1. The following equilibria are given:

$$N_2 + 3H_2 \overset{K_1}{\rightleftharpoons} 2NH_3$$

$$N_2 + O_2 \overset{K_2}{\rightleftharpoons} 2NO$$

$$H_2 + \frac{1}{2}O_2 \overset{K_3}{\rightleftharpoons} H_2O$$

The equilibrium constant of the reaction $2NH_3 + \frac{5}{2}O_2 \rightleftharpoons 2NO + 3H_2O$ in terms of K_1, K_2 and K_3 is **(IIT-JEE 2003)**

(A) $\dfrac{K_1K_2}{K_3}$ (B) $\dfrac{K_1K_3^2}{K_2}$

(C) $\dfrac{K_2K_3^3}{K_1}$ (D) $K_1K_2K_3$

Solution

(C) The reaction can be rearranged and summed to obtain the resultant reaction as

$$\begin{array}{ll} 2NH_3 \rightleftharpoons N_2 + 3H_2 & (1/K_1) \\ 3H_2 + \frac{3}{2}O_2 \rightleftharpoons 3H_2O & (K_3)^3 \\ N_2 + O_2 \rightleftharpoons 2NO & K_2 \\ \hline 2NH_3 + \frac{5}{2}O_2 \rightleftharpoons 2NO + 3H_2O & \end{array}$$

The equilibrium constant is $\dfrac{K_2(K_3)^3}{K_1}$.

2. Which is correct statement if N_2 is added at equilibrium condition?

(A) The equilibrium will shift to forward direction because according to the second law of thermodynamics the entropy must increases in the direction of spontaneous reaction.

(B) The condition for equilibrium is $G_{N_2} + 3G_{H_2} = 2G_{NH_3}$ where G is Gibbs energy per mole of the gaseous species measured at that partial pressure. The condition of equilibrium is unaffected by the use of catalyst, which increases the rate of both the forward and reverse reactions to the same extent.

(C) The catalyst will increase the rate of forward reaction by α and that of reverse reaction by β.

(D) The catalyst will not alter the rate of either of the reaction. **(IIT-JEE 2006)**

Solution

(B) This is because change in Gibbs energy is given by:

$$\Delta G(\text{reaction}) = \Delta G(\text{products}) - \Delta G(\text{reactants})$$

Also, catalyst only speeds up the reaction without affecting the equilibrium conditions.

3. The equilibrium $2Cu \rightleftharpoons Cu + Cu$ in aqueous medium at 25°C shifts towards the left in the presence of

(A) NO_3^- (B) Cl^-

(C) SCN^- (D) CN^- **(IIT-JEE 2011)**

Solution

(B, C, D) The reaction of Cu^{2+} ions with CN^-, SCN^- and $CuCl_2$ will lead to the formation of $[Cu(CN)_4]^{3-}$, $[Cu(SCN)_4]^{3-}$ and CuCl which will shift the reaction in the reverse direction.

$$Cu^{2+} + 2CN^- \rightleftharpoons Cu(CN)_2$$
$$2Cu(CN)_2 \rightleftharpoons 2CuCN + (CN)_2$$
$$CuCN + 3CN^- \rightleftharpoons [Cu(CN)_4]^{3-}$$
$$Cu^{2+} + 4SCN^- \rightleftharpoons [Cu(SCN)_4]^{3-}$$
$$CuCl_2 + Cu \rightleftharpoons 2CuCl$$

4. The thermal dissociation equilibrium of $CaCO_3(s)$ is studied under different conditions

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

For this equilibrium, the correct statement(s) is (are)

(A) ΔH is dependent on T.

(B) K is independent of the initial amount of $CaCO_3$.

(C) K is dependent on the pressure of CO_2 at a given T.

(D) ΔH is independent of catalyst, if any.

(JEE Advanced 2013)

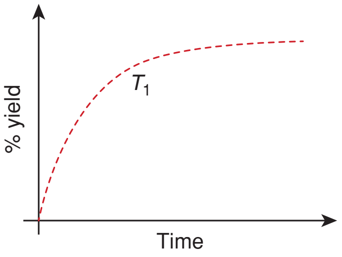
Solution

(D) For the reaction $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$, ΔH is dependent on temperature according to Kirchhoff's equation $\Delta H_2 - \Delta H_2 = C_p(T_2 - T_1)$, but it is independent of addition of catalyst.
The equilibrium constant (K) is independent of initial amount of $CaCO_3$ and pressure of CO_2 at a given temperature.

5. The % yield of ammonia as a function of time in the reaction

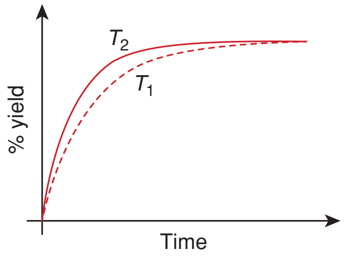
$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g), \Delta H < 0$$

at (p, T_1) is given below,

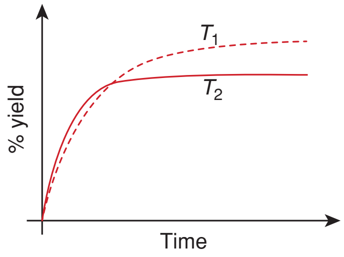


If this reactions is conducted at (p, T_2), with $T_2 > T_1$, the % yield of ammonia as a function of time is represented by

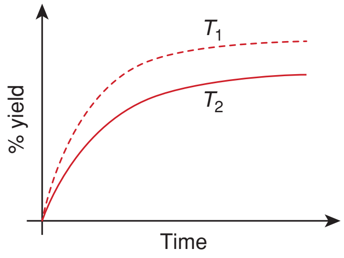
(A)



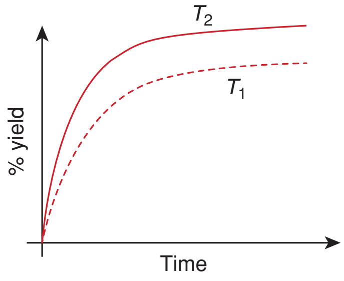
(B)



(C)



(D)



(JEE Advanced 2015)

Solution

(B) The equilibrium yield of ammonia gets lowered with the increase of temperature. However, at higher temperature the initial rate of forward reaction would be greater than at lower temperature that is why the percentage yield of NH_3 would be more initially.

6. Consider the reaction equilibrium, $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ with $\Delta H^\circ = -198$ kJ. On the basis of Le Chatelier's principle, the condition favorable for forward reaction is **(AIEEE 2003)**

(A) lowering of temperature as well as pressure.
(B) increasing temperature as well as pressure.
(C) lowering the temperature and increasing the pressure.
(D) any value of temperature and pressure.

Solution

(C) According to Le Chatelier's principle, for an exothermic reaction, on lowering the temperature will shift the reaction in forward direction. Also, as the number of gaseous moles is decreasing, so on increasing the pressure, the reaction will shift in forward direction.

7. For the reaction equilibrium, $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ the concentrations of N_2O_4 and NO_2 at equilibrium are 4.8×10^{-2} and 1.2×10^{-2} mol L^{-1}, respectively. The value of K_C for the reaction is **(AIEEE 2003)**

(A) 3.3×10^{-2} mol L^{-1}
(B) 3×10^{-1} mol L^{-1}
(C) 3×10^{-3} mol L^{-1}
(D) 3×10^{3} mol L^{-1}

Solution

(C) The equilibrium concentration is

$$K_C = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(1.2\times10^{-2})^2}{(4.8\times10^{-2})} = 3\times10^{-3}\ \text{mol L}^{-1}$$

8. What is the equilibrium expression for the reaction $P_4(s) + 5O_2(g) \rightleftharpoons P_4O_{10}(s)$?

(A) $K_C = \frac{[P_4O_{10}]}{[P_4][O_2]^5}$
(B) $K_C = \frac{1}{[O_2]^5}$
(C) $K_C = [O_2]^5$
(D) $K_C = \frac{[P_4O_{10}]}{5[P_4][O_2]}$

Solution

The equilibrium constant is given by $K_C = \frac{[P_4O_{10}]}{[P_4][O_2]^5}$.

As the concentration of solids is taken as unity, we have

$$K_C = \frac{1}{[O_2]^5}$$

9. For the reaction $CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$ the ratio K_p/K_C is equal to **(AIEEE 2004)**

(A) $(1/RT)$
(B) 1.0
(C) $\sqrt{RT}$
(D) RT

Solution

(A) We know that $K_p = K_C\,(RT)^{\Delta n}$ where Δn = number of moles of products in gaseous phase − number of moles of reactants in gaseous phase = $1 - 2 = -1$

Substituting, we get $\quad K_p = K_C(RT)^{-1} \Rightarrow \frac{K_p}{K_C} = \frac{1}{RT}$

10. The equilibrium constant for the reaction $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ at temperature T is 4×10^{-4}. The value of K_C for the reaction $NO(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{1}{2}O_2(g)$ at the same temperature is **(AIEEE 2004, 2012)**

(A) 2.5×10^2
(B) 0.02
(C) 4×10^{-4}
(D) 50

Solution

(D) Consider the reaction $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ where given $K_C = 4 \times 10^{-4}$. Reversing the equation and dividing it throughout by 2, we get

$$NO(g) \rightarrow \tfrac{1}{2}N_2(g) + \tfrac{1}{2}O_2(g)$$

The new equilibrium constant is

$$K'_C = \left(\frac{1}{K_C}\right)^{1/2} = \left(\frac{1}{4\times10^{-4}}\right)^{1/2} = 50$$

11. In a cell that utilizes the reaction $Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$, addition of H_2SO_4 to cathode compartment, will **(AIEEE 2004)**

(A) lower the E and shift equilibrium to the left.
(B) increases the E and shift equilibrium to the left.
(C) increase the E and shift equilibrium to the right.
(D) lower the E and shift equilibrium to the right.

Solution

(C) This is because according to Le Chatelier's principle, increase in H^+ ions will shift the equilibrium in the forward direction.

12. An amount of solid NH_4SH is placed in a flask already containing ammonia gas at a certain temperature and 0.50 atm pressure. Ammonium hydrogen sulphide decomposes to yield NH_3 and H_2S gases in the flask. When the decomposition reaction reaches equilibrium, the total pressure in the flask rises to 0.84 atm. The equilibrium constant for NH_4SH decomposition at this temperature is **(AIEEE 2005)**

(A) 0.30 (B) 0.18
(C) 0.17 (D) 0.11

Solution

(D) The reaction involved is

$$\begin{array}{lccc} & NH_4HS & \rightleftharpoons NH_3(g) & + H_2S(g) \\ \text{Initial pressure} & p_0 & 0.5 & 0 \\ \text{Pressure at equilibrium} & p_0 - p & 0.5 + p & p \end{array}$$

The total pressure at equilibrium is $0.5 + 2x = 0.84$ (given)
Solving, we get $x = 0.17$. Therefore,

$$K_p = p_{NH_3} \times p_{H_2S} = (0.67) \times (0.17) = 0.1139$$

13. The exothermic formation of CF_3 is represented by the equation:

$$Cl_2(g) + 3F_2(g) \rightleftharpoons 2ClF_3(g); \quad \Delta_r H = -329 \text{ kJ}$$

Which of the following will increase the quantity of ClF_3 in an equilibrium mixture of Cl_2, F_2 and ClF_3?

(A) Increasing the temperature
(B) Removing Cl_2
(C) Increasing the volume of the container
(D) Adding F_2 **(AIEEE 2005)**

Solution

(D) According to Le Chatelier's principle, on increasing the concentration of reactants (i.e., adding F_2) will shift the equilibrium in the forward direction.

14. For the reaction $2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$, $K_C = 1.8 \times 10^{-6}$ at 184°C and $R = 0.0821$ kJ mol^{-1} K^{-1}. When K_p and K_C are compared at 184°C it is found that **(AIEEE 2005)**

(A) K_p is greater than K_C
(B) K_p is less than K_C
(C) $K_p = K_C$
(D) Whether K_p is greater than, less than or equal to K_C depends upon the total gas pressure.

Solution

(A) We know that $K_p = K_C (RT)^{\Delta n}$
where Δn = number of moles of products in gaseous phase – number of moles of reactants in gaseous phase $= 3 - 2 = 1$
Substituting, we get $K_p = K_C(RT) \Rightarrow K_p > K_C$

15. Phosphorus pentachloride dissociates as follows, in a closed reaction vessel, $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$. If total pressure at equilibrium of the reaction mixture is p and degree of dissociation of PCl_5 is x, the partial pressure of PCl_3 will be **(AIEEE 2006)**

(A) $\left(\dfrac{x}{x+1}\right)p$ (B) $\left(\dfrac{2x}{1-x}\right)p$
(C) $\left(\dfrac{x}{x-1}\right)p$ (D) $\left(\dfrac{x}{1-x}\right)p$

Solution

(A) The reaction can be represented as

$$\begin{array}{lccc} & PCl_5(g) & \rightleftharpoons PCl_3(g) & + Cl_2(g) \\ \text{Initial moles} & 1 & 0.5 & 0 \\ \text{Moles at equilibrium} & 1 - x & x & x \end{array}$$

The total number of moles at equilibrium $= 1 - x + x + x = 1 + x$
Therefore, the partial pressure of PCl_3 is

$$p_{(PCl_3)} = \left(\frac{x}{x+1}\right)p$$

16. The equilibrium for the reaction $SO_3(g) \rightleftharpoons SO_2(g) + \frac{1}{2}O_2(g)$ is $K_C = 4.9 \times 10^{-2}$. The value of K_C for the reaction $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ will be **(AIEEE 2006)**

(A) 416 (B) 2.40×10^{-3}
(C) 9.8×10^{-2} (D) 4.9×10^{-2}

Solution

(A) For $SO_2 + \frac{1}{2}O_2 \rightleftharpoons SO_3 \quad K'_C = (1/K_C)$

For $2SO_2 + O_2 \rightleftharpoons 2SO_3 \quad K'_C = (1/K_C)^2$

The equilibrium constant is

$$K'_C = \left(\frac{1}{4.9 \times 10^{-2}}\right)^2 = \frac{10^4}{4.9 \times 4.9} = \frac{10000}{24.01} = 4.1649 \times 100 = 416.49$$

17. The equilibrium constants K_{p_1} and K_{p_2} for the reactions $X \rightleftharpoons 2Y$ and $Z \rightleftharpoons P + Q$, respectively, are in the ratio of 1:9. If the degree of dissociation of X and Z be equal, then the ratio of total pressure at these equilibria is

(A) 1:36 (B) 1:1 (C) 1:3 (D) 1:9 **(AIEEE 2008)**

Solution

(A) The reaction can be expressed as

	$X \rightleftharpoons 2Y$	
Initial moles	1	0
Moles at equilibrium	$(1-\alpha)$	2α

Now, the enthalpy of the reaction is

$$\Delta H = \frac{\Delta H_1}{2} + \Delta H_2 + \Delta H_3 = \frac{240}{2} - 349 - 381$$
$$= -610 \text{ kJ mol}^{-1}$$

Therefore, $K_{p_1} = \dfrac{(2\alpha)^2}{(1-\alpha)}\left(\dfrac{p_1}{1+\alpha}\right)^1$

The other reaction can be expressed as

	$Z \rightleftharpoons P + Q$		
Initial moles	1	0	0
Moles at equilibrium	$(1-\alpha)$	α	α

Here, $K_{p_2} = \dfrac{x^2}{(1-\alpha)}\left(\dfrac{p_2}{1+\alpha}\right)^1$

Given that the ratio of equilibrium constants is

$$\frac{K_{p_1}}{K_{p_2}} = \frac{1}{9}$$

Therefore, the ratio of their pressures is

$$\frac{4\times p_1}{p_2} = \frac{1}{9} \Rightarrow \frac{p_1}{p_2} = \frac{1}{36}$$

18. For the following three reactions A, B and C, the equilibrium constants are given:

A. $CO(g) + H_2O(g) \xrightleftharpoons{K_1} CO_2(g) + H_2(g)$

B. $CH_4(g) + H_2O(g) \xrightleftharpoons{K_2} CO(g) + 3H_2(g)$

C. $CH_4(g) + 2H_2O(g) \xrightleftharpoons{K_3} CO_2(g) + 4H_2(g)$

Which of the following relations is correct?

(A) $K_1(K_2)^{1/2} = K_3$ (B) $K_2K_3 = K_1$

(C) $K_3 = K_1K_2$ (D) $K_3(K_2)^3 = (K_1)^2$

(AIEEE 2008)

Solution

(C) The expression for K_3 is

$$K_3 = \frac{[CO_2][H_2]^4}{[CH_4][H_2O]^2}$$

which can be obtained by $K_1 \times K_2$

$$K_2 \times K_1 = \frac{[CO_2][H_2]}{[CO][H_2O]} \times \frac{[CO][H_2]^3}{[CH_4][H_2O]}$$
$$= \frac{[CO_2][H_2]^4}{[CH_4][H_2O]^2} = K_3$$

19. A vessel at 100 K contains CO_2 with a pressure of 0.5 atm. Some of the CO_2 is converted into CO on the addition of graphite. If the total pressure at equilibrium is 0.8 atm, the value of K_p is

(A) 3 atm (B) 0.3 atm

(C) 0.18 atm (D) 1.8 atm **(AIEEE 2011)**

Solution

(D) The reaction can be expressed as

	$CO_2(g)$	$+ C \rightleftharpoons$	$2CO(g)$
Initial moles	p	p	0
Moles at equilibrium	$p-x$	$p-x$	$2x$

Total pressure at equilibrium = 0.8 atm (given)
Total number of moles at equilibrium $= p - x + 2x = p + x$
Also, since $p \propto n$,

$$\frac{p}{p+x} = \frac{0.5}{0.8}$$

Solving, we get $x = 0.3$. Now,

$$K_p = \frac{p_{CO}^2}{p_{CO_2}}$$

where $p_{CO_2} = p - x = 0.5 - 0.3 = 0.2$ atm and $p_{CO} = 2x = 2 \times 0.3 = 0.6$. Therefore,

$$K_p = \frac{0.6\times 0.6}{0.2} = 1.8 \text{ atm}$$

20. The following reaction is performed at 298 K.

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

The standard free energy of formation of NO(g) is 86.6 kJ/mol at 298 K. What is the standard free energy of formation of NO_2(g) at 298 K? ($K_p = 1.6 \times 10^{12}$)

(A) $86600 + R(298) \ln (1.6 \times 10^{12})$

(B) $86600 - \dfrac{\ln(1.6\times 10^{12})}{R(298)}$

(C) $0.5[2 \times 86{,}600 - R(298) \ln (1.6 \times 10^{12})]$

(D) $R(298) \ln(1.6 \times 10^{12}) - 86600$

(JEE Main 2015)

Solution

(C) $\Delta G^\circ = 2\Delta G^\circ_{(NO_2)} - [2\Delta G^\circ_{(NO)} + \Delta G^\circ_{(O_2)}]$

$= 2x - [2\times 86{,}600 + 0]$

Also, $\Delta G^\circ = -RT \ln K_p$

$-R(298)\ln(1.6\times 10^{12}) = 2x - 2\times 86{,}600$

$x = 0.5[2\times 86600 - R(298)\ln(1.6\times 10^{12}]$

21. The standard Gibbs energy change at 300 K for the reaction $2A \rightleftharpoons B + C$ is 2494.2 J. At a given time, the composition of the reaction mixture is $[A] = \dfrac{1}{2}$, [B] = 2 and $[C] = \dfrac{1}{2}$. The reaction proceeds in the:
[$R = 8.314$ J/K/mol, $e = 2.718$]

(A) reverse direction because $Q > K_C$

(B) forward direction because $Q < K_C$

(C) reverse direction because $Q < K_C$

(D) forward direction because $Q > K_C$

(JEE Main 2015)

Solution

(A) We know that

$$Q = \frac{[C][B]}{[A]^2} = \frac{\left(\frac{1}{2}\right)(2)}{\left(\frac{1}{2}\right)^2} = 4$$

Using the equation,

$$\Delta G = \Delta G^\circ + RT\ln Q = 2494.2 + 8.314 \times 300 \ln 4$$

we would get a positive quantity. Now, $\Delta G^\circ = RT\ln K_C$. So, $\Delta G = RT\ln(Q/K_C)$.

As ΔG is positive, so $Q > K_C$ and thus the reaction shifts in the reverse direction.

REVIEW QUESTIONS

1. Explain why pure liquids and solids can be ignored while writing the equilibrium constant expression.

2. What is the difference between a heterogeneous equilibrium and a homogeneous equilibrium?

3. The ester, ethyl acetate, is formed by the reaction of ethanol and acetic acid and the equilibrium is represented as:

$$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$$

(a) Write the concentration ratio, Q_C, for this reaction. Note that water is not in excess and is not a solvent in this reaction.

(b) At 293 K, if one starts with 1.000 mol of acetic acid and 1.180 mol of ethanol, there is 0.171 mol of ethyl acetate in the final equilibrium mixture. Calculate the equilibrium constant.

(c) Starting with 0.500 mol of ethanol and 1.000 mol of acetic acid and maintaining it at 293 K, 0.214 mol of ethyl acetate is found after some time. Has equilibrium been reached?

(d) We do not use dilute aqueous solutions for this reaction. Why?

(e) Why is some concentrated sulphuric acid usually added to reaction mixture in the laboratory preparation of ethyl acetate.

(f) Since the heat of reaction is nearly zero for this reaction, how will the equilibrium constant depend upon the temperature?

4. Define physical equilibrium with examples.

5. For the exothermic formation of sulphur trioxide from sulphur dioxide and oxygen in the gas phase:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

$K_p = 40.5$ atm^{-1} at 900 K and $\Delta_r H = -198$ kJ mol^{-1}

(a) Write the expression for the equilibrium constant for the reaction.

(b) At room temperature (≈300 K) will K_p be greater than, less than or equal to K_p at 900 K.

(c) How will the equilibrium be affected if the volume of the vessel containing the three gases is reduced, keeping the temperature constant. What happens?

(d) What is the effect of adding 1 mol of He(g) to a flask containing SO_2, O_2 and SO_3 at equilibrium at constant temperature.

6. Why doesn't a catalyst affect the position of equilibrium in a chemical reaction?

7. Under what conditions will the following reactions go in the forward direction?

(a) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) + 45\text{ kcal} + 45\text{ kcal}.$

(b) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g) + 27.8\text{ kcal}$

(c) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g) - X\text{ kcal}$

8. Consider the following equilibrium.

$$2NaHCO_3(s) \rightleftharpoons Na_2CO_3(s) + CO_2(g) + H_2O(g)$$

If you were converting between K_p and K_C, what value of Δn_g would you use?

9. How will the value of K_p for the following reactions be affected by an increase in temperature?

(a) $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)\ \Delta H^\circ = -18\text{ kJ}$

(b) $N_2O(g) + NO_2(g) \rightleftharpoons 3NO(g)\ \Delta H^\circ = +155.7\text{ kJ}$

(c) $2NO(g) + CI_2(g) \rightleftharpoons 2NOCI(g)\ \Delta H^\circ = -77.07\text{ kJ}$

10. Write the equilibrium law for each of the following gaseous reactions in terms of molar concentrations and partial pressures.

(a) $2PCl_3(g) + O_2(g) \rightleftharpoons 2POCl_3(g)$

(b) $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$

(c) $N_2H_4(g) + 2O_2(g) \rightleftharpoons 2NO(g) + 2H_2O(g)$

(d) $N_2H_4(g) + 6H_2O_2(g) \rightleftharpoons 2NO_2(g) + 8H_2O(g)$

(e) $SOCl_2(g) + H_2O(g) \rightleftharpoons SO_2(g) + 2HCl(g)$

11. How will the position of equilibrium in the following reaction

$$\text{Heat} + CH_4(g) + 2H_2S(g) \rightleftharpoons CS_2(g) + 4H_2(g)$$

be affected by: **(a)** adding $CH_4(g)$, **(b)** adding $H_2(g)$, **(c)** removing $CS_2(g)$, **(d)** decreasing the volume of the container and **(e)** increasing the temperature?

12. Two 1.00 L bulbs are filled with 0.500 atm of $F_2(g)$ and $PF_3(g)$, as illustrated in Fig. 9.8. At a particular temperature, $K_p = 4.0$ for the reaction of the gases to form $PF_5(g)$:

$$F_2(g) + PF_3(g) \rightleftharpoons PF_5(g)$$

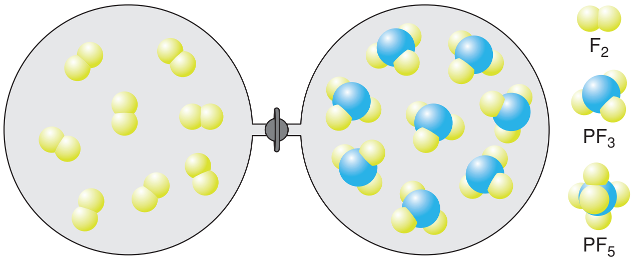


Figure 9.8

(a) The stopcock between the bulbs is opened and the pressure falls. Make a sketch of this apparatus showing the gas composition once the pressure is stable.

(b) List any chemical reactions that continue to occur once the pressure is stable.

(c) Suppose all the gas in the left bulb is forced into the bulb on the right and then the stopcock is closed. Make a second sketch to show the composition of the gas mixture after equilibrium is reached. Comment on how the composition of the one-bulb system differs from that for the two-bulb system.

13. Use the following equilibria

$$2CH_4(g) \rightleftharpoons C_2H_6(g) + H_2(g) \qquad K_C = 9.5 \times 10^{-13}$$

$$CH_4(g) + H_2O(g) \rightleftharpoons CH_3OH(g) + H_2(g) \quad K_C = 2.8 \times 10^{-21}$$

to calculate K_C for the reaction

$$2CH_3OH(g) + H_2(g) \rightleftharpoons C_2H_6(g) + 2H_2O(g)$$

14. Define the state of equilibrium. What are the general characteristics of the following equilibria?

(a) Solid–liquid

(b) Liquid–vapor

(c) Solid–vapor

15. What are the general characteristics of equilibrium involving physical processes?

16. What are reversible and irreversible reactions? Give one example of each.

17. State the law of mass action.

18. The equilibrium constant of a reaction is 2 × 10^{-3} at 25 °C and 2 × 10^{-2} at 50 °C. Is the reaction exothermic or endothermic?

19. Deduce the expression for equilibrium constant using the law of mass action.

20. What qualitative information can you obtain from the magnitude of equilibrium constant?

21. For the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, at 400 K, K_p = 41. Find the value of K_p for each of the following reactions at the same temperature:

(a) $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$

(b) $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$

(c) $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$

22. Why does manufacture of ammonia by Haber's process require higher pressure, low temperature, use of catalyst?

23. Using Le Chatelier's principle, explain the effect of pressure on the solubility of gases in liquids.

NUMERICAL PROBLEMS

1. Nitrous oxide, N_2O, sometimes called laughing gas has a strong tendency to decompose into nitrogen and oxygen following the equation

$$2N_2O(g) \rightleftharpoons 2N_2(g) + O_2(g)$$

but the reaction is so slow that the gas appears to be stable at room temperature (25°C). The decomposition reaction has $K_C = 7.3 \times 10^{34}$. What is the value of K_p for this reaction at 25°C?

2. 0.96 g of HI were heated to attain equilibrium $2HI \rightleftharpoons H_2 + I_2$. The reaction mixture on titration requires 15.7 mL of *N*/10 hypo solution. Calculate the degree of dissociation of HI.

3. N_2O_4 dissociates as $N_2O_4 \rightleftharpoons 2NO_2$. At 55°C and 1 atm, the percentage dissociation is 50.3%. At what pressure and same temperature, the equilibrium mixture will have the ratio of N_2O_4: NO_2 as 1:8?

4. One mole of each $Cl_2(g)$ and $Br_2(g)$ were taken in a 2 L flask, sealed and heated to some temperature where the following equilibrium was established and at equilibrium, the mole% of ClBr(g) was 40%.

$$Cl_2(g) + Br_2(g) \rightleftharpoons 2BrCl(g) \qquad (1)$$

At equilibrium, 2 mol of NO gas was added where the following additional equilibrium was established.

$$2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g) \qquad (2)$$

At new equilibrium, mixture was found to contain 0.9 mol of BrCl(g). Determine K_C for the two equilibria in Eq. (1) and (2).

5. At a certain temperature, K_C = 4.50 for the reaction

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

If 0.300 mol of N_2O_4 is placed into a 2.00 L container at that temperature, what will be the equilibrium concentrations of both gases?

6. The standard Gibbs energy change for a reaction is ΔG^o = –41.8 kJ mol^{-1} at 700 K and 1 atm. Calculate the equilibrium constant of the reaction at 700 K.

7. The reaction $NO_2(g) + NO(g) \rightleftharpoons N_2O(g) + O_2(g)$ has $\Delta G^o_{1273} = -9.67$ kJ. A 1.00 L reaction vessel at 1000 °C contains 0.0200 mol NO_2, 0.040 mol NO, 0.015 mol N_2O and 0.0350 mol O_2. Is the reaction at equilibrium? If not, in which direction will the reaction proceed to reach equilibrium.

8. Four moles of hydrogen iodide are taken in a 10 L flask and kept at 800 K. It undergoes the following decomposition reaction until the equilibrium is attained. The equilibrium mixture is found to contain 0.42 mol of iodine. Calculate the equilibrium constant of the reaction.

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

9. Five grams of PCl_5 were completely vaporized at 250°C in a vessel of 1.9 L capacity. The mixture at equilibrium exerted a pressure of one atmosphere. Calculate the degree of dissociation, K_C and K_p for this reaction.

10. The equilibrium constant for the reaction, $I_2(s) + Br_2(g) \rightleftharpoons 2IBr(g) \rightleftharpoons$ is 0.164 at 25°C.

(a) Bromine gas is introduced into a container with excess solid iodine. The pressure and temperature are 0.164 atm and 25°C. Find the partial pressure of IBr formed at equilibrium. Assume that the vapor pressure of $I_2(s)$ is negligible.

(b) Calculate $\Delta G°$ for the above reaction.

11. Equilibrium constant, K_C for the reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ at 500 K is 0.061. At a particular time, the analysis shows that composition of the reaction mixture is 3.00 mol L^{-1} N_2, 2.00 mol L^{-1} H_2, and 0.500 mol L^{-1} NH_3. Is the reaction at equilibrium? If not, in which direction does the reaction tend of proceed to reach equilibrium?

12. The reaction $CuSO_4{\cdot}3H_2O(s) \rightleftharpoons CuSO_4{\cdot}H_2O(s)$; the dissociation pressure is 7×10^{-3} atm at 25°C and $\Delta H° = 2750$ cal. What will be the dissociation pressure at 127°C?

13. The vapor density of a mixture of NO_2 and N_2O_4 is 38.3 at 27°C. Calculate the number of moles of NO_2 in 100 g mixture at equilibrium.

14. At 500°C, the decomposition of water into hydrogen and oxygen,

$$2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$$

has $K_C = 6.0 \times 10^{-28}$. How many moles of H_2 and O_2 are present at equilibrium in a 5.00 L reaction vessel at that temperature if the container originally held 0.015 mol H_2O?

15. At 460°C, the reaction $SO_2(g) + NO_2(g) \rightleftharpoons NO(g) + SO_3(g)$ has $K_C = 85.0$. Suppose 0.100 mol of SO_2, 0.0600 mol of NO_2, 0.0800 mol of NO, and 0.120 mol of SO_3 are placed in a 10.0 L container at that temperature. What will the concentrations of all the gases be when the system reaches equilibrium?

16. One mole of nitrogen is mixed with three moles of hydrogen in a 4 L container. If 0.25% of nitrogen is converted to ammonia by the following reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$. Calculate the equilibrium constant (K_C) in concentration units. What will be the value of K_C for the following equilibrium?

$$\tfrac{1}{2}N_2(g) + \tfrac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$$

17. Air containing 79% of nitirogen and 21% of oxygen by volume is heated at 2200 K and 1 atm until equilibrium is established according to the reaction $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$. If the K_p the reaction is 1.1×10^{-3}, calculate the amount of nitric oxide produced in terms of volume percent.

18. N_2O_4 is 25% dissociated at 37°C and one atmospheric pressure. Calculate: (a) K_p for $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ and (b) % dissociation at 37°C and 0.1 atm.

19. If a mixture of N_2 and H_2 in the ratio 1:3 at 50 atmosphere and 650°C is allowed to react till equilibrium is reached. Ammonia present at equilibrium was at 25 atm pressure. Calculate the equilibrium constant for the reaction. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$.

20. At 473 K, equilibrium constant K_C for decomposition of PCl_5 is 8.3×10^{-3}. If enthalpy for the reaction is 124.0 kJ mol^{-1}

(a) what is the value of K_C for reverse reaction?

(b) what would be the affect on K_C if (i) more PCl_5 is added, (ii) pressure is increased or (iii) temperature is increased?

21. At 540 K, 0.10 mole of PCl_5 are heated in a 8 L flask. The pressure of the equilibrium mixture is found to be 1.0 atm. Calculate K_p and K_C for reaction. **(IIT-JEE 1998)**

22. The K value for the reaction: $H_2 + I_2 \rightleftharpoons 2HI$, at 460°C is 49. If the initial pressure of H_2 and I_2 is 0.5 atm respectively, determine the partial pressure of each gas at equilibrium. **(IIT-JEE 1999)**

23. Calculate the value of log K for the reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ at 25°C. The standard enthalpy of formation of $NH_3(g)$ is –46 kJ and standard entropies of $N_2(g)$, $H_2(g)$ and $NH_3(g)$ are 191,130,192 J K^{-1} mol^{-1} respectively. ($R = 8.314$ J $K^{-1}mol^{-1}$) **(IIT-JEE 1999)**

24. The value of K_p is 1×10^{-3} atm^{-1} at 25°C for the reaction: $2NO + Cl_2 \rightleftharpoons 2NOCl$. A flask contains NO at 0.02 atm and at 25°C. Calculate the mol of Cl_2 that must be added if 1% of the NO is to be converted to NOCl at equilibrium. The volume of the flask is such that 0.2 mol of gas produce 1 atm pressure at 25°C. (Ignore probable association of NO to N_2O_2.) **(IIT-JEE 2001)**

25. The equilibrium constant K_C for the reaction $N_2O_4 \rightleftharpoons 2NO_2$ in chloroform at 291 K is 1.14. Calculate the free energy change of the reaction when the concentration of the two gases is 0.5 mol dm^{-3} each at the same temperature. ($R = 0.082$ L atm K^{-1} mol^{-1}).

ADDITIONAL OBJECTIVE QUESTIONS

Single Correct Choice Type

1. Equilibrium constants are given (in atm) for the following reactions at 0°C

$$SrCl_2 \cdot 6H_2O(s) \rightleftharpoons SrCl_2 \cdot 2H_2O(s) + 4H_2O(g)$$
$$K_p = 6.89 \times 10^{-12}$$

The vapor pressure of water at 0°C is 4.58 torr. Calculate the pressure of water vapor in equilibrium at 0°C

(A) 2.6×10^{-3} atm
(B) 1.62×10^{-3} atm
(C) 1.20×10^{-4} atm
(D) 4.28×10^{-3} atm

2. Predict which of the following reaction will have appreciable concentration of reactants and products:

(A) $Cl_2(g) \rightleftharpoons 2Cl(g);\quad K_C = 5 \times 10^{-39}$
(B) $Cl_2(g) + 2NO(g) \rightleftharpoons 2NOCl(g);\quad K_C = 3.7 \times 10^{8}$
(C) $Cl_2(g) + 2NO_2(g) \rightleftharpoons 2NO_2Cl(g);\quad K_C = 1.8$
(D) All of these

3. $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ When 46 g I_2 and 1 g of H_2 are heated, an equilibrium is reached at 450°C. The equilibrium mixture contained 1.9g of I_2. How many moles of I_2 and HI are present at equilibrium?
(A) 0.0075 and 0.147 mol (B) 0.0050 and 0.147 mol
(C) 0.0075 and 0.347 mol (D) 0.0052 and 0.347 mol

4. The partial pressures of CH_3OH, CO and H_2 in the equilibrium mixture for the reaction $CO + 2H_2 \rightleftharpoons CH_3OH$ at 427°C are 2.0, 1.0 and 0.1 atm respectively. The value of K_p for the decomposition of CH_3OH into CO and H_2 is
(A) 1×10^2atm (B) 2×10^2atm^{-1}
(C) 50 atm^2 (D) 5×10^{-3}atm^2

5. Consider the following equilibrium in a closed container $N_2O_4(g) \rightleftharpoons 2NO_2(g)$. At a fixed temperature, the volume of the reaction container is halved, for this change, which of the following statements holds true regarding the equilibrium constant (K) and degree of dissociation (α):
(A) neither K_p nor α changes
(B) both K and α changes
(C) K_p changes but α does not
(D) K does not change but α changes

6. For the reaction $2NO_2(g) + O_2(g) \rightleftharpoons N_2O_5(g)$. If the equilibrium constant is K_p, then the equilibrium constant for the reaction $2N_2O_5(g) \rightleftharpoons 4NO_2 + O_2(g)$ would be
(A) K_p^2 (B) $\dfrac{2}{K_p}$
(C) $\dfrac{1}{K_p^2}$ (D) $\dfrac{1}{\sqrt{K_p}}$

7. A container whose volume is V, contains an equilibrium mixture that consists of 2 mol each of PCl_5, PCl_3 and Cl_2 (all gases). The pressure is 30.3975 kPa and temperature is T. A certain amount of $Cl_2(g)$ is now introduced keeping the pressure and temperature constant until the equilibrium volume changes to $2V$. Calculate the amount of Cl_2 that was added
(A) 10/3 mol (B) 20/3 mol
(C) 1/3 mol (D) 1/4 mol

8. For a certain equilibrium, over the temperature range 500 K to 700 K, the equilibrium constant, K_p confirms to the equation log

$$K_p = 30.1 - \frac{6.36 \times 10^3}{T} - 5.7 \log T$$

Calculate $\Delta G°$ at 600 K.
(A) −16.04 kcal mol^{-1} (B) −14.60 kcal mol^{-1}
(C) −10.064 kcal mol^{-1} (D) −14.00 kcal mol^{-1}

9. If PCl_5 is 80% dissociated at 523 K. Calculate the vapor density of the equilibrium mixture at 523 K.
(A) 75.9 (B) 57.9
(C) 97.5 (D) 95.7

10. In the melting of ice, which one of the conditions will be more favorable?
(A) High temperature and high pressure
(B) Low temperature and low pressure
(C) Low temperature and high pressure
(D) High temperature and low pressure

11. Example of physical equilibria is
(A) $H_2 + I_2 \rightleftharpoons 2HI$ (B) $CaCO_3 \rightleftharpoons CaO + CO_2$
(C) $H_2O(s) \rightleftharpoons H_2O(l)$ (D) $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

12. For the reaction $2SO_2$ (g) + O_2(g) $\rightleftharpoons$ $2SO_3$(g) the partial pressure of SO_2, O_2 and SO_3 are 0.559, 0.101 and 0.331 atm, respectively. What would be the partial pressure of O_2 gas, to get equal moles SO_2 and SO_3.
(A) 0.188 atm (B) 0.288 atm
(C) 0.388 atm (D) 0.488 atm

13. When ethanol and acetic acid were mixed together in equimolecular proportion 66.6% are converted into ethyl acetate. Calculate K_C. Also calculate quantity of ester produced if one mole of acetic acid is treated with 0.5 mol and 4 mol of alcohol, respectively.
(A) 4, 0.93, 0.43 (B) 0.93, 4, 0.43
(C) 0.43, 0.93,4 (D) 4, 0.43, 0.93

14. Calculate the temperature at which the product gases at equilibrium at 1 atm will contain 400 ppm (parts per million) of carbon monoxide.
(A) 399K (B) 400K
(C) 275K (D) 200K

15. For the reversible reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ at 500°C, the value of K_p is 1.44×10^{-5} when partial pressure is measured in atmospheres. The corresponding value of K_C, with concentration in mole L^{-1}, is
(A) $\dfrac{1.44 \times 10^{-5}}{(0.082 \times 500)^{-2}}$ (B) $\dfrac{1.44 \times 10^{-5}}{(8.314 \times 773)^{-2}}$
(C) $\dfrac{1.44 \times 10^{-5}}{(0.082 \times 773)^{2}}$ (D) $\dfrac{1.44 \times 10^{-5}}{(0.082 \times 773)^{-2}}$

16. Le Chatelier's principle is applicable to
(A) only homogeneous chemical reversible reaction.
(B) only heterogeneous chemical reversible reaction.
(C) only physical equilibria.
(D) all systems chemical or physical, in equilibrium.

17. At temperature T, a compound $AB_2(g)$ dissociates according to the reaction $2AB_2(g) \rightleftharpoons 2AB(g) + B_2(g)$ with degree of dissociation α, which is small compared with unity. The expression for K_p, in terms of α and the total pressure, p_T is
(A) $\dfrac{p_T\alpha^3}{2}$ (B) $\dfrac{p_T\alpha^2}{3}$
(C) $\dfrac{p_T\alpha^2}{2}$ (D) None of these

18. Starting with 3:1 mixture of H_2 and N_2 at 450°C, the equilibrium mixture is found to be 9.6% NH_3, 22.6% N_2 and 67.8% H_2 by volume. The total pressure is 50 atm. What will be the value of K_p. The reaction is $N_2 + 3H_2 \rightleftharpoons 2NH_3$
(A) 3.25×10^{-5} atm^{-2} (B) 5.23×10^{-5} atm^{-2}
(C) 6.23×10^{-2} atm^{-2} (D) 8×10^{-5} atm^{-2}

19. Find out the value of K_C for each of the following equilibria from the value of K_p:

(i) $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$; $K_p = 1.8 \times 10^{-2}$ at 500 K

(ii) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$; $K_p = 167$ at 1073 K the value of K_C are, respectively

(A) 4.4×10^{-4} and 1.90
(B) 8.8×10^{-4} and 3.8
(C) 4.4×10^{-4} and 1.90
(C) 8.8×10^{4} and 3.8

20. At constant temperature, the equilibrium constant (K) for the decomposition reaction $N_2O_4(x/2) \rightleftharpoons 2NO_2$ is expressed by

$$K_p = \frac{4x^2 p}{(1 - x^2)}$$

where p = pressure, x = extent of decomposition. Which one of the following statements is true?

(A) K increases with increase of p
(B) K increases with increase of x
(C) K increases with decrease of x
(D) K remains constant with change in p and x

21. The vapor density of N_2O_4 at a certain temperature is 30. The percentage dissociation of N_2O_4 at this temperature is

(A) 55.5%
(B) 60%
(C) 70%
(D) 53.3%

22. The equilibrium constant of the reaction $A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$ at 100°C is 50. If 1 L flask containing one mole of A_2 is connected to a 2 L flask containing two moles of B_2, the number of moles of AB formed at 373 K will be

(A) 1.886
(B) 2.317
(C) 0.943
(D) 18.86

23. NO and Br_2 at initial partial pressure of 98.4 and 41.3 torr, respectively, were allowed to react at 300 K. At equilibrium, the total pressure was 110.5 torr. Calculate the value of K_p for the following reaction at 300 K.

$$2NO(g) + Br(g) \rightleftharpoons 2NOBr(g)$$

(A) 124
(B) 134
(C) 154
(D) 174

24. In the equilibrium $SO_2Cl_2 \rightleftharpoons SO_2 + Cl_2$ at 2000 K and 10 atm pressure, % Cl_2 = % SO_2 = 40 by volume. Then

(A) $K_p = 2$ atm
(B) $\dfrac{n(SO_2Cl_2)}{n(SO_2)} = \dfrac{1}{4}$ at equilibrium
(C) $K_p = 8$ atm
(D) $n(SOCl_2) = n(SO_2) = n(Cl_2)$

25. At a certain temperature, the equilibrium constant K_C is 16 for the reaction, $SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$. If 1.0 mol each of all the four gases is taken in a 1 L container the concentration of NO_2 at equilibrium would be

(A) 1.6 mol L^{-1}
(B) 0.8 mol L^{-1}
(C) 0.4 mol L^{-1}
(D) 0.6 mol L^{-1}

26. In a system $A(s) \rightleftharpoons 2B(g) + 3C(g)$. If the concentration of C at equilibrium is increased by a factor 2, it will cause the equilibrium concentration of B to change to

(A) two times of its original value.
(B) one half of its original value.
(C) $2\sqrt{2}$ times of its original value.
(D) $1/2\sqrt{2}$ times of its original value.

27. For the chemical reaction, $3X(g) + Y(g) \rightleftharpoons X_3Y(g)$ the amount of X_3Y at equilibrium is affected by:

(A) temperature and pressure.
(B) temperature only.
(C) pressure only.
(D) temperature, pressure and catalyst.

28. In the reaction, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ the concentration of H_2, I_2 and HI at equilibrium are 8.0, 3.0 and 28 mol L^{-1}, respectively. What will be the equilibrium constant?

(A) 30.61
(B) 32.66
(C) 29.40
(D) 20.90

29. When two reactants, A and B are mixed to give product C and D_3 the reaction quotient question at the initial stages of the reaction

(A) is zero.
(B) decrease with time.
(C) is independent of time.
(D) increase with time.

30. What will be the equilibrium constant at 500°C, if heat of reaction in this temperature range is −105185.8 J.

(A) 0.144×10^{-4} atm
(B) 0.144×10^{-3} atm
(C) 0.144×10^{-2} atm
(D) 0.144×10^{-1} atm

31. The following reactions are known to occur in the body $CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^{-1}$. If CO_2 escapes from the system

(A) pH will decrease.
(B) hydrogen ion concentration will diminish.
(C) H_2CO_3 concentration will remain unchanged.
(D) The forward reaction will be favored.

32. For the reaction: $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$, the degree of dissociation (α) of HI(g) is related to equilibrium constant, K_p by the expression

(A) $\dfrac{1 + 2\sqrt{K_p}}{2}$
(B) $\sqrt{\dfrac{1 + 2K_p}{2}}$
(C) $\sqrt{\dfrac{2K_p}{1 + 2K_p}}$
(D) $\dfrac{2\sqrt{2K_p}}{1 + 2\sqrt{K_p}}$

33. For which of the following reactions, the degree of dissociation cannot be calculated from the vapor density data

(I) $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$
(II) $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$
(III) $2NO(g) \rightleftharpoons N_2(g) + O_2(g)$
(IV) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

(A) I and III
(B) II and IV
(C) I and II
(D) III and IV

34. An example of reversible reaction is

(A) $Pb(NO_3)_2 + 2NaI = PbI_2 + 2NaNO_3$
(B) $AgNO_3 + HCl = AgCl + HNO_3$
(C) $2Na + 2H_2O = 2NaOH + H_2$
(D) $KNO_3 + NaCl = KCl + NaNO_3$

35. For the reaction, $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$, at a given temperature the equilibrium amount of CO_2 (g) can be increased by

(A) adding a suitable catalyst.
(B) adding an inert gas.
(C) decreasing the volume of the container.
(D) increasing the amount of CO(g).

36. A reaction mixture containing H_2, N_2 and NH_3 has partial pressures 2 atm, 1 atm and 3 atm, respectively, at 725 K. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ is 4.28×10^{-5} atm^{-2} at 725 K, in which direction the net reaction will go?

(A) Forward
(B) Backward
(C) No net reaction
(D) Cannot be predicted

37. Ammonium hydrogen sulphide dissociates according to the equation $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$. If the observed pressure of the mixture is 1.12 atm at 106°C, what is the equilibrium constant K_p of the reaction?

(A) 0.3136 atm^2
(B) 2 atm^2
(C) 1 atm^2
(D) 0.4842 atm^2

38. When sulphur in the form of S_8 is heated at 900 K, the initial pressure of one atm falls by 29% at equilibrium. This is because of conversion of some S_8 to S_2. Find the value of equilibrium constant for this reaction.

(A) 1.16 atm^3
(B) 0.71 atm^3
(C) 2.55 atm^3
(D) 5.1 atm^3

39. $BiCl_3(g) + H_2O(g) \rightleftharpoons BiOCl(s) + 2HCl(g)$ in the above system at equilibrium, the pressure of water vapor is doubted. The new equilibrium partial pressure of HCl increases

(A) 1.73 times
(B) 1.414 times
(C) 2.0 times
(D) 1.0 times

40. K_1 and K_2 are equilibrium constant for reactions

(I) $N_2(g) + O_2(g) \rightarrow 2NO(g)$

(II) $NO(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{1}{2}O_2(g)$

Then, from (I) and (II)

(A) $K_I = \left(\frac{1}{K_{II}}\right)^2$
(B) $K_I = K_{II}^2$
(C) $K_I = \frac{1}{K_{II}}$
(D) $K_I = (K_{II})^0$

41. If a mixture of 0.482 mol N_2 and 0.933 mol of O_2 is placed in a 10 L reaction vessel and allowed to form N_2O at a temperature for which $K_C = 2.0 \times 10^{-37}$. The composition of equilibrium mixture are

(A) N_2 = 0.482 mol L^{-1}, O_2 = 0.0933 mol L^{-1}, N_2O = 6.6×10^{-21} mol L^{-1}
(B) N_2 = 0.482 mol L^{-1}, O_2 = 0.933 mol L^{-1}, N_2O = 6.6×10^{-21} mol L^{-1}
(C) N_2 = 0.0482 mol L^{-1}, O_2 = 0.0933 mol L^{-1}, N_2O = 6.6×10^{-21} mol L^{-1}
(D) N_2 = 0.0482 mol L^{-1}, O_2 = 0.0931 mol L^{-1}, N_2O = 8.8×10^{-21} mol L^{-1}

42. One of the reaction that takes place in producing steel from iron ore is the reduction of iron(II) oxide by carbon monoxide to give iron metal and carbon dioxide is

$$FeO(s) + CO(g) \rightleftharpoons Fe(s) + CO_2(g); \quad K_p = 0.265 \text{ atm}$$

at 1050 K. What are the equilibrium partial pressures of CO and CO_2, respectively, at 1050 K if the initial partial pressures are: $p_{CO} = 1.4$ atm and $p_{CO_2} = 0.80$ atm?

(A) $p_{CO} = 1.739$ atm and $p_{CO_2} = 0.461$ atm
(B) $p_{CO} = 17.39$ atm and $p_{CO_2} = 0.461$ atm
(C) $p_{CO} = 1.79$ atm and $p_{CO_2} = 0.46$ atm
(D) $p_{CO} = 2.739$ atm and $p_{CO_2} = 1.461$ atm

43. What are the values of ΔG^o and the equilibrium constant for the formation of NO_2 from NO and O_2 at 298 K

$$NO(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO_2(g)$$

where $\Delta G_f^o(NO_2) = 52.0\,kJ\,mol^{-1}$, $\Delta G_f^o(NO) = 87.0\,kJ\,mol^{-1}$, $\Delta G_f^o(O_2) = 0\,kJ\,mol^{-1}$

(A) 35 kJ mol^{-1} and 1.365×10^6
(B) –35 kJ mol^{-1} and 1.365×10^{-6}
(C) –350kJ mol^{-1} and 1.3×10^6
(D) –35 kJ mol^{-1} and 1.365×10^6

44. A reversible chemical reaction having two reactants in equilibrium. If the concentration of the reactants is doubled, then the equilibrium constant will

(A) also be doubled.
(B) be halved.
(C) become one-fourth.
(D) remain the same.

Multiple Correct Choice Type

1. Solid ammonium carbamate, $NH_4CO_2NH_2(s)$, dissociates into ammonia and carbon dioxide when it evaporates as shown by $NH_4CO_2NH_2(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$. At 25°C, the total pressure of the gases in equilibrium with the solid is 0.116 atm. If 0.1 atm of CO_2 is introduced after equilibrium is reached then

(A) final pressure of CO_2 will be less than 0.1 atm.
(B) final pressure of CO_2 will be more than 0.1 atm.
(C) pressure of NH_3 will decrease due to addition of CO_2.
(D) pressure of NH_3 will increase due to addition of CO_2.

2. The equilibrium of which of the following reaction will not be disturbed by the addition of an inert gas at constant volume?

(A) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
(B) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$
(C) $CO_2(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$
(D) $C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$

3. Consider the reactions given below. In which cases, will the reaction proceed towards the right by increasing the pressure?

(A) $4HCl(g) + O_2(g) \rightarrow 2Cl_2(g) + 2H_2O(g)$
(B) $Cl_2(g) + H_2O(g) \rightarrow 2HCl(g) + \frac{1}{2}O_2(g)$
(C) $CO_2(g) + 4H_2(g) \rightarrow CH_4(g) + 2H_2O(g)$
(D) $N_2(g) + O_2(g) \rightarrow 2NO(g)$

4. For the reaction $2A(g) + B(g) \rightleftharpoons 2C(g)$; $\Delta H = +13.6$ kJ, which of the following will increase the extent of the reaction at equilibrium
(A) increasing the temperature.
(B) increasing the pressure.
(C) addition of catalyst.
(D) removing C.

5. The following reaction attains equilibrium at high temperature

$$N_2(g) + 2H_2O(g) + \text{heat} \rightleftharpoons 2NO(g) + 2H_2(g)$$

The yield of NO is affected by
(A) increasing the nitrogen concentration.
(B) decreasing the hydrogen concentration.
(C) compressing the reaction mixture.
(D) none of these.

6. If K_1 and K_2 are the equilibrium constants at temperature T_1 and T_2 and $T_2 > T_1$ then
(A) when $\Delta H = 0$; $K_2 = K_1$
(B) when $\Delta H > 0$; $K_2 > K_1$
(C) when $\Delta H < 0$; $K_2 < K_1$
(D) when $\Delta H > 0$; $K_2 < K_1$

7. $2CaSO_4(s) \rightleftharpoons 2CaO(s) + O_2(g)$, $\Delta H > 0$. Above equilibrium is established by taking sufficient amount of $CaSO_4(s)$ in a closed container at 1600 K. Then which of the following may be correct option? (Assume that solid $CaSO_4$ is present in the container in each case.)
(A) Moles of CaO(s) will increase with the increase in temperature
(B) If the volume of the container is doubled at equilibrium then partial pressure of $SO_2(g)$ will change at new equilibrium.
(C) If the volume of the container is halved partial pressure of $O_2(g)$ at new equilibrium will remain same
(D) If two moles of the He gas is added at constant pressure than the moles of CaO(s) will increase.

8. In presence of a catalyst, what happens to the chemical equilibrium?
(A) Energy of activation of the forward and backwards reactions are lowered by same amount.
(B) Equilibrium amount is not disturbed.
(C) Rates of forward and reverse reaction increase by the same factor.
(D) More product is formed.

9. 138 g of $N_2O_4(g)$ is placed in 8.2 L container at 300 K. The equilibrium vapor density of mixture was found to be 30.67. Then ($R = 0.082$ L atm mol^{-1} K^{-1})
(A) α = degree of dissociation of $N_2O_4 = 0.25$.
(B) K_p of $N_2O_4 \rightleftharpoons 2NO_2(g)$ will be 9 atm.
(C) Total pressure at equilibrium mixture will be 6.75 atm.
(D) The density of equilibrium mixture will be 16.83 g L^{-1}.

10. $N_2F_4 \rightleftharpoons 2NF_2(g)$; $\Delta H^\circ = 38.5$ kJ. Which of the following conditions will favor the formation of NF_2?
(A) Adding He to the equilibrium mixture at constant temperature and volume.
(B) Increasing the temperature.
(C) NF_2 gas is removed from the reaction mixture.
(D) Decreasing the pressure at constant temperature.

11. Consider the following equilibria:

(I) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

(II) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

(III) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

Choose the correct statement(s):
(A) Addition of an inert gas at constant volume has no effect on all the three equilibria.
(B) Addition of an inert gas at constant pressure favors the forward reaction in (III), backward reaction in (I) and has no effect on (II).
(C) Addition of an inert gas at constant pressure has no effect on equilibrium (II), but favors the forward reaction in (I) and backward reaction in (III).
(D) Addition of inert gas has no effect on all the three equilibria at constant temperature and also at constant pressure.

12. The reactions in which the yield of the products cannot be increased by the application of high pressure
(A) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
(B) $NH_4HS\ (s) \rightleftharpoons NH_3(g) + H_2S(g)$
(C) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$
(D) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

13. Which of the following statements about the reaction quotient, Q, are correct?
(A) The reaction quotient, Q, and the equilibrium constant always have the same numerical value
(B) Q may be $>$ or $<$ or $= K_C$
(C) Q (numerical value) varies as reaction proceeds
(D) $Q = 1$ at equilibrium

14. Consider the exothermic reaction

$$CoCl_4^{2-}(aq) + 6H_2O(l) \rightleftharpoons [Co(H_2O)_6]^{2+}(aq) + 4Cl^-(aq)$$

[Consider initially only $CoCl_4^{2-}$ is added to water]
(A) If HCl is added to above equilibrium then concentration of $CoCl_4^{2-}(aq)$ will increase
(B) On dilution with water the concentration of $CoCl_4^{2-}(aq)$ will decrease
(C) On doubling the volume of solution by addition water the final concentration of $[Co(H_2O)_6]^{2+}$ will be more than its initial concentration
(D) On increasing temperature the concentration of $CoCl_4^{2-}$ will decrease

15. For the equilibrium $N_2O_4 \rightleftharpoons 2NO_2$, the value of equilibrium constant is 2×10^{-4} at a particular temperature if equilibrium is established by taking 2 mol of N_2O_4 in 1 L container then approximately, the
(A) concentration of NO_2 at equilibrium is 0.02 M.
(B) concentration of NO_2 at equilibrium is 0.01 M.
(C) concentration of N_2O_4 at equilibrium is 2 M.
(D) concentration of N_2O_4 at equilibrium is 1 M.

16. Which of the following relationship(s) describe the quantitative effect of temperature on the equilibrium constant?

(A) $\dfrac{d\ln K_p}{dT} = \dfrac{\Delta H}{RT^2}$ (B) $\dfrac{d\ln K_p}{dT} = \dfrac{\Delta E}{RT^2}$

(C) $\dfrac{d\ln K_C}{dT} = \dfrac{\Delta E}{RT^2}$ (D) $\dfrac{d\ln K_C}{dT} = \dfrac{\Delta H}{RT^2}$

Assertion–Reasoning Type

Choose the correct option from the following:

(A) Statement 1 is True, Statement 2 is True; Statement 2 is a correct explanation for Statement 1.
(B) Statement 1 is True, Statement 2 is True; Statement 2 is NOT a correct explanation for Statement 1.
(C) Statement 1 is True; Statement 2 is False.
(D) Statement 1 is False; Statement 2 is True.

1. Statement 1: Addition of an inert gas at constant pressure to dissociation equilibrium of $PCl_5 \rightleftharpoons PCl_3(g) + Cl_2(g)$ favors forward reaction.

Statement 2: $K_C = \dfrac{\alpha^2 V}{1-\alpha}$ for dissociation equilibrium of PCl_5, where α is degree of dissociation of PCl_5.

2. Statement 1: In the Haber process $N_2 + 3H_2 \rightleftharpoons 2NH_3$; $\Delta H < 0$. Then concentration of NH_3 increases by decreasing the temperature and increasing the pressure.

Statement 2: For an exothermic reaction, equilibrium constant increase by increasing the temperature.

3. Statement 1: The equilibrium amount of NO will be less with increase in temperature.

Statement 2: Heat is absorbed by increasing the temperature and the equilibrium shifts towards left.

4. Statement 1: $\Delta G = \Delta G^\circ + 2.303RT\log_{10}Q$, where Q is reaction quotient.

Statement 2: Q may be greater or lesser than K or equal to K if $\Delta G = 0$.

5. Statement 1: Pure liquids and solids can be ignored while writing the equilibrium constant expression.

Statement 2: The concentration of pure liquids and solids does not remain constant.

6. Statement 1: The equilibrium constant for a reaction having positive ΔH° increase with increase of temperature.

Statement 2: The temperature dependence of the equilibrium constant is related to ΔH° and not ΔS° for the reaction.

7. Statement 1: The equilibrium attained in a closes vessel remains unaltered by the addition of $CaCO_3(s)$ is as follows: $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2\uparrow$

Statement 2: Heterogeneous reaction is unaffected by solid and liquid.

8. Statement 1: $SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g) + \text{heat}$

Forward reaction is favored at high temperature and low pressure.

Statement 2: Reaction is exothermic.

Comprehension Type

Read the paragraphs and answer the questions that follow.

Paragraph I

The difference in free energy of the reaction when all the reactants and products are in STP (1 atm and 298 K) is ΔG° and K_C and K_p are the thermodynamic equilibrium constants of the reaction. The relation between them is as follows:

$$\Delta G^\circ = -2.303RT\log K_C$$

and $\Delta G^\circ = -2.303RT\log K_p$ (in case of ideal gas)

This equation relates the equilibrium constant of a reaction to a thermodynamic property. It is sometimes easier to calculate the free energy in a reaction rather than to measure the equilibrium constant. The standard free energy change can be calculated as

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

where ΔH° is the standard enthalpy change and ΔS° is the standard entropy change.

1. Which of the following statement is correct for a reversible process in state of equilibrium

(A) $\Delta G = -2.303RT\log K$ (B) $\Delta G = 2.303RT\log K$
(C) $\Delta G^\circ = -2.303RT\log K$ (D) $\Delta G^\circ = 2.303RT\log K$

2. Calculate the equilibrium concentration ratio of C to A if 2.0 mol each of A and B were allowed to come to equilibrium at 300 K

$$A + B \rightleftharpoons C + D \qquad \Delta G^\circ = 460\ \text{Cal}$$

(A) 1.0 (B) 0.5
(C) 0.8 (D) 0.679

3. At 490°C, the value of equilibrium constant; K_p is 45.9 the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

Calculate, the value of ΔG° for the reaction at that temperature

(A) –3.5 kcal (B) 3.5 kcal
(C) 5.79 kcal (D) –5.79 kcal

Paragraph II

Chemical equilibrium is a dynamic state in which the composition of a system does not change, and net reaction is zero. In reversible reactions, a stage is reached when the rate of transformation of reactants into products equals the rate of transformation of products into reactants. At this stage, the composition of reactants and products does not change with time. The reaction has not stopped, but the rates of forward and reverse reactions are equal. For a general reaction $A(g) + B(g) \rightleftharpoons C(g) + D(g)$, we have

$$K_C = \frac{[C][D]}{[A][B]} \quad \text{and} \quad K_p = \frac{p_C \times p_D}{p_A \times p_B}$$

where K_C is equilibrium constant when the ratio of the concentrations of the product to reactants and K_p is the equilibrium constant for the ratio of partial pressure and of products to reactants. The relation between K_p and K_C is as follows.

$$K_p = K_C(RT)^{\Delta n}$$

4. The mass ratio of steam and hydrogen is found to be 1:2 at equilibrium.

$$3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$$

The value of equilibrium constant (K_C) for the above reaction is

(A) 3.05×10^3 (B) 1.05×10^5
(C) 0.75×10^2 (D) 2.42×10^7

5. For the reaction $NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$, the equilibrium constant $K_p = 2.9 \times 10^{-5}$ atm^3. The total pressure of gases at equilibrium when 1 mole of reactant was heated will be

(A) 0.0194 atm (B) 0.0388 atm
(C) 0.0580 atm (D) 0.0667 atm

6. K_C for the reaction $\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) + \frac{1}{2}Br_2(g) \rightleftharpoons NOBr(g)$ from the following information at 298 K

$$2NO(g) \rightleftharpoons N_2(g) + O_2(g); \quad K_1 = 2.4 \times 10^{30}$$

$$NO(g) + \tfrac{1}{2}Br_2(g) \rightleftharpoons NOBr(g); \quad K_2 = 1.4$$

(A) 3.15×10^{-9} (B) 6.35×10^{-18}
(C) 9.03×10^{-16} (D) 17×10^{-17}

7. The equilibrium constant for the reaction $2SO_2 + O_2 \rightleftharpoons 2SO_3$ at 1000 K is 3.5. What would the partial pressure of oxygen gas have to be to give equal moles of SO_2 and SO_3?

(A) 0.29 atm (B) 3.5 atm
(C) 0.53 atm (D) 1.87 atm

Paragraph III

In dissociation reactions involving gaseous molecules, the total mass remains same and the number of moles increases as a result of the reaction. Hence, the average molecular weight and vapor density decrease. So, the volume increases at constant temperature and pressure and hence the vapor density decreases. The relationship between initial vapor density and that at equilibrium can be found as follows:

At constant temperature and constant pressure for a fixed mass of gaseous mixtures.

$$\text{Vapor density} \propto \rho \propto \frac{1}{V}$$

Now, for ideal gas, $pV = nRT$ or volume ∝ number of moles. So,

$$\text{Vapor density} \propto \frac{1}{\text{Number of moles}} \Rightarrow \frac{D}{D_0} = \frac{n}{n_0}$$

where D_0 and D are the vapor densities in the beginning and at equilibrium and n_0 and n are the number of moles in the beginning and at equilibrium. The vapor densities of PCl_5 at 200°C and 252°C are 70.2 and 57.2, respectively, at 1 atm.

8. From the given data, it can be interpreted that

(A) If degree of dissociation is more, then vapor density is more for PCl_5.
(B) More the degree of dissociation, less is the vapor density of PCl_5.
(C) Degree of dissociation and vapor density cannot be correlated.
(D) α is independent of temperature.

9. X, Y and Z react in the 1:1:1 stoichiometric ratio. The concentration of X, Y and Z were found to vary with time as shown in Fig. 9.9.

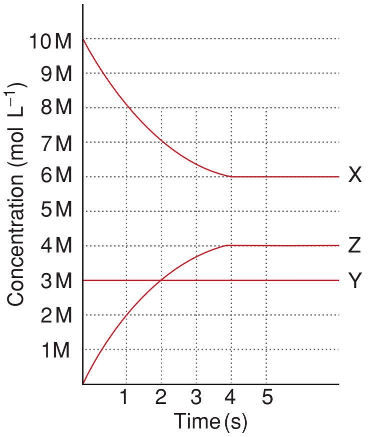


Figure 9.9

Which of the following equilibrium reaction represents the correct variation of concentration with time?

(A) $X(g) + Y(g) \rightleftharpoons Z(g)$ (B) $X(g) + Y(s) \rightleftharpoons Z(g)$
(C) $Z(g) + Y(s) \rightleftharpoons X(g)$ (D) $Z(g) + X(g) \rightleftharpoons Y(g)$

10. Value of the equilibrium constant (K_C) for the equilibrium represented in above graph will be

(A) $\frac{9}{2}$ (B) $\frac{21}{4}$ (C) $\frac{2}{3}$ (D) $\frac{12}{7}$

11. If above equilibrium is established in a 2 L container by taking reactants in sufficient amount then how many moles of component Y must have reacted to establishment the equilibrium.

(A) 0 (B) 6 (C) 12 (D) 8

Integer Answer Type

The answer is a **non-negative integer**.

1. For the reaction:

$$CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$$

K is 0.63 at 700°C and 1.66 at 1000°C. The average ΔH° for the temperature range considered is __________.

2. Equilibrium constant for the reaction $A_3(g) + 3B_2(g) \rightleftharpoons 3AB_2(g)$ is 64.0. Then the equilibrium constant for the reaction $\frac{1}{3}A_3(g) + B_2(g) \rightleftharpoons AB_2(g)$ will be __________.

3. When NO and NO_2 are mixed, the following equilibria are readily obtained;

$$2NO_2 \rightleftharpoons N_2O_4;\ K_p = 6.8\ \text{atm}^{-1} \text{ and } NO + NO_2 \rightleftharpoons N_2O_3$$

In an experiment when NO and NO_2 are mixed in the ratio of 1:2, the find total pressure was 5.05 atm and the partial pressure of $N_2O_4$was 1.7 atm. Calculate the equilibrium partial pressure of NO in atmosphere.

4. Ammonium carbamate when heated to 200°C gives a mixture of vapors ($NH_2COONH_4 \rightleftharpoons 2NH_3 + CO_2$) with a density 13.0. The degree of dissociation of ammonium carbamate is __________.

5. For the equilibrium $N_2O_4 \rightleftharpoons 2NO_2$, $(\Delta G^{o}_{N_2O_4})_{298\,K} = 100$ kJ mol^{-1} and $(\Delta G^{o}_{NO_2})_{298\,K} = 50$ kJmol^{-1} When 5 mol L^{-1} of each in taken, calculate the value of ΔG for the reaction at 298 K.

6. If concentrations of SO_2 and O_2 in the equilibrium reaction, $2SO_2(g)+O_2(g) \rightleftharpoons 2SO_3(g)$ are quadrupled, the concentration of SO_3 now will be __________ times.

7. For the reaction involving oxidation of ammonia by oxygen to form nitric oxide and water vapor, the equilibrium constant has the units (bar)^n. Then n is __________.

Matrix–Match Type

1. Match the reactions with the relations of equilibrium constants

Column I	Column II
(A) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$	(p) $K_p = K_c(RT)$
(B) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	(q) $K_p = K_c(RT)^2$
(C) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$	(r) $K_p = K_c(RT)^{-2}$
(D) $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$	(s) $K_p = K_c$
	(t) $K_p = K_c(RT)^{-1}$

2. Match the relation with the prediction of equilibrium.

Column I	Column II
(A) $Q = K$	(p) Reaction is nearer to completion
(B) $Q < K$	(q) Reaction is not at equilibrium
(C) $Q > K$	(r) Reaction is fast in forward direction
(D) $K >> 1$	(s) Reaction at equilibrium
	(t) Rate of forward reaction = rate of back ward reaction

3. Match the chemical reaction in equilibrium with the pressure dependent of degree of dissociation of the reaction:

Column I	Column II
(A) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	(p) $\alpha \propto \sqrt{p}$
(B) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$	(q) $\alpha \propto \sqrt{1/p}$
(C) $PCl_5(g) \rightleftharpoons PCl_3(g)+Cl_2(g)$	(r) $\alpha \propto p$
(D) $N_2+O_2 \rightleftharpoons 2NO$	(s) $\alpha \propto p^0$
	(t) $K_p = K_C$

4. Match the effect of change administered to its the effect on equilibrium.

Column I	Column II
(A) For the equilibrium $NH_4I(s) \rightleftharpoons NH_3(g) + HI(g)$, pressure is increased at equilibrium	(p) Forward shift
(B) For the equilibrium $N_2 + 3H_2 \rightleftharpoons 2NH_3$, volume is increased at equilibrium	(q) No change
(C) For the equilibrium $H_2O(g) + CO(g) \rightleftharpoons H_2(g) + CO_2(g)$, inert gas is added at constant pressure at equilibrium	(r) Backward shift
(D) For the equilibrium $PCl_5 \rightleftharpoons PCl_3 + Cl_2$, Cl_2 is removed at equilibrium	(s) Final pressure is more than initial pressure

5. Match the quantity with the effect/relation.

Column I	Column II
(A) $K_C<1$	(p) Affected by temperature
(B) Degree of dissociation	(q) Affected by pressure
(C) Equilibrium constant	(r) $K_f<K_b$
(D) Melting of ice	(s) $K_f>K_b$

ANSWERS

Review Questions

1. The molar concentrations of pure solids and liquids is constant, so molar concentrations are constant and not mentioned in equilibrium constant expression.

2. Reactants and products are in same phase in homogeneous, whereas in different phases in heterogeneous.

3. **(a)** $Q_C = \dfrac{[CH_3COOC_2H_5(l)][H_2O(l)]}{[CH_3COO(l)][C_2H_5OH(l)]}$; **(b)** 3.92; **(c)** 0.20; **(d)** none or very little amount of ester will be formed if dilute aqueous solutions are used in this reaction; **(e)** it acts as a catalyst and is a dehydrating agent; **(f)** Variation would be small with change in temperature.

5. **(a)** $K_p = \dfrac{p^2_{SO_3}(g)}{p^2_{SO_2(g)} \times p_{O_2(g)}}$; **(b)** greater; **(c)** it will shift the equilibrium to the right; **(d)** no effect.

6. Catalyst affects both the forward and the reverse reaction to the same extent.

7. **(a)** Low temperature, high pressure, excess of O_2 and SO_2
(b) Low temperature, high pressure, excess of NO and O_2
(c) High temperature, low pressure, excess of PCl_5

8. 2 mol
9. **(a)** Decreases; **(b)** increases; **(c)** decreases.
11. The system shifts to **(a)** right; **(b)** left; **(c)** right; **(d)** left; **(e)** right.
13. $K_C = 1.2 \times 10^{29}$
18. Endothermic
21. **(a)** 1/41; **(b)** $(41)^{1/2}$; **(c)** $(41)^2$

Numerical Problems

1. 1.8×10^{36}
2. 0.209 or 20.9%
3. 0.19 atm
4. $K_{C(1)} = 1.78$ and $K_{C(2)} = 86$
5. $[N_2O_4] = 0.016$ M; $[NO_2] = 0.268$ M
6. $K = 1.312 \times 10^4$
7. Forward
8. 0.01767
9. 0.843; $K_C = 0.0565$
10. **(a)** 0.1014 atm; **(b)** 4.48 kJ
11. No
12. 1.26×10^{-2} atm
13. 0.434 mol
14. $[H_2] = 2.2 \times 10^{-11}$ mol; $[O_2] = 1.1 \times 10^{-11}$ mol
15. $[SO_2] = 0.0046$ M; $[NO_2] = 0.00058$ M; $[NO] = 0.0134$ M; $[SO_3] = 0.0174$ M
16. 1.49×10^{-5} L^2 mol^{-2}, 3.86×10^{-3} L mol^{-1}
18. **(a)** 0.267 atm; **(b)** 63.26 %
19. 1.677×10^{-3}
17. 1.33%
20. **(a)** 120.48; **(b)** (i,ii) same; (iii) increase
21. $K_C = 4 \times 10^{-2}$ mol L^{-1}; $K_p = 1.77$ atm
22. $p_H = 0.11$ atm; $p_{I_2} = 0.11$ atm; $p_{HI} = 0.78$ atm
23. $\log K = 5.845$
24. 0.0204 mol
25. –19.67 L atm

Additional Objective Questions

Single Correct Choice Type

1. (B) **2.** (C) **3.** (C) **4.** (B) **5.** (D)
6. (C) **7.** (B) **8.** (C) **9.** (B) **10.** (A)
11. (C) **12.** (B) **13.** (D) **14.** (A) **15.** (B)
16. (D) **17.** (A) **18.** (B) **19.** (A) **20.** (D)
21. (D) **22.** (A) **23.** (B) **24.** (C) **25.** (C)
26. (D) **27.** (A) **28.** (B) **29.** (D) **30.** (A)
31. (B) **32.** (D) **33.** (A) **34.** (D) **35.** (D)
36. (B) **37.** (A) **38.** (C) **39.** (B) **40.** (A)
41. (C) **42.** (A) **43.** (D) **44.** (D)

Multiple Correct Choice Type

1. (B, C) **2.** (A, B, C, D) **3.** (A, C) **4.** (B, C, D) **5.** (A, B, C)
6. (A, B, C) **7.** (A, C, D) **8.** (A, B, C) **9.** (B, C, D) **10.** (B, C, D)
11. (A, B) **12.** (B, C) **13.** (B, C) **14.** (A, B, D) **15.** (B, C)
16. (A, C)

Assertion–Reasoning Type

1. (C) **2.** (C) **3.** (A) **4.** (B) **5.** (C)
6. (B) **7.** (A) **8.** (D)

Comprehension Type

1. (C) **2.** (D) **3.** (D) **4.** (B) **5.** (C)
6. (C) **7.** (A) **8.** (B) **9.** (B) **10.** (C)
11. (D)

Integer Answer Type

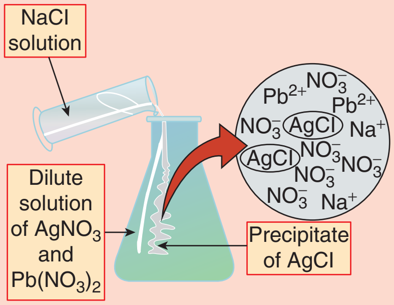
1. (8) **2.** (4) **3.** (2) **4.** (1) **5.** (4)
6. (8) **7.** (1)

Matrix–Match Type

1. A → (s); B → (r); C → (p); D → (q)
2. A → (s, t); B → (q, r); C → (q); D → (p)
3. A → (r); B → (p); C → (q); D → (s, t)
4. A → (r, s); B → (r); C → (q); D → (p, s)
5. A → (r); B → (p, q); C → (p); D → (p, q)

10

Ionic Equilibrium


NaCl solution
Dilute solution of AgNO3 and Pb(NO3)2
Pb2+ NO3− Pb2+ NO3− AgCl Na+ AgCl NO3− NO3− NO3− NO3− Na+
Precipitate of AgCl

Selective precipitation

Contents

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10.5 Relative Strength of Acids and Bases
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The equilibrium established between ionized and non-ionized species is known as **ionic equilibrium**. A number of equilibria involving ions are known to exist. Substances that form ions in aqueous solutions or in fused state are called **electrolytes**.

Consider the aqueous solutions of sugar and common salt. The former does not conduct electricity, whereas solution of salt (sodium chloride) conducts electricity and the conductance is found to increase with increase in concentration of sodium chloride. Based on this, Michael Faraday defined electrolytes as substances that furnish ions in their aqueous solution and conduct electricity. The substances that do not conduct electricity in their aqueous solutions are called **non-electrolytes** and some examples are cane sugar, carbon tetrachloride, benzene, etc.

10.1 | WEAK AND STRONG ELECTROLYTES

Electrolytes that conduct electricity in their fused state are known as **true electrolytes**. These exist in ionic state, that is, as cations and anions in their pure normal states and conduct electricity in their molten state. For example, sodium chloride and potassium chloride exist as Na^+Cl^- and K^+Cl^- ions in their normal states and conduct electricity in fused state. By analogy, substances that conduct electricity only in aqueous solutions are called **potential electrolytes** and examples are acetic acid, ammonia, etc. Electrolytes are classified as strong or weak electrolytes based on their tendency to ionize or their extent of ionization.

1. Substances such as NaCl, HCl, H_2SO_4, KOH, etc. that ionized almost completely are known as **strong electrolytes**. These electrolytes dissociate completely into their ions in aqueous solutions and are hence good conductors of electricity and so

chemical equilibrium has relevance for them. Examples of strong electrolytes are sodium chloride, potassium chloride, sodium oxide, potassium sulphate, potassium nitrate, etc.

2. Substances such as CH_3COOH, NH_4OH, etc. that ionize to a small extent are known as **weak electrolytes**. These electrolytes are partly ionized in their aqueous solutions, so an equilibrium is established between ions and dissociated molecules. The law of chemical equilibrium can thus be applied to study the behavior of weak electrolytes in solutions. For example, acetic acid (CH_3COOH), HCN, etc.

10.2 | IONIZATION OF ELECTROLYTES

According to Arrhenius theory of electrolytic dissociation, when an electrolyte is dissolved in water, it dissociates into positive and negative ions that move freely in the bulk of the solution. The number of positive ions is equal to the number of negative ions formed, so the solution remains electrically neutral. The ionized ions have a tendency to recombine back to the unionized electrolyte, thus a dynamic equilibrium exists between ionized and unionized electrolytes. For example, for a binary electrolyte AB

$$\mathrm{AB} \rightleftharpoons \mathrm{A}^+ + \mathrm{B}^-$$

Applying law of mass action, the ionization constant is given by

$$K = \frac{[\mathrm{A}^+][\mathrm{B}^-]}{[\mathrm{AB}]}$$

The fraction of electrolyte dissociated into ions at equilibrium out of the total number of molecules of electrolyte dissolved is known as degree of dissociation or ionization and is given by

$$\alpha = \frac{\text{Number of molecules present as ions}}{\text{Total number of molecules of the electrolyte}}$$

The extent of dissociation increases with increase in dilution and degree of dissociation of an electrolyte at infinite dilution is assumed to be unity (i.e. $\alpha = 1$).

The equivalence conductance of electrolytes depends on the number of ions. As the degree of dissociation increases with dilution, the equivalent conductance also increases and becomes constant at infinite dilution.

Ostwald's Dilution Law

Consider a binary electrolyte AB, in aqueous solution, which dissociates as follows:

$$\mathrm{AB} \rightleftharpoons \mathrm{A}^+ + \mathrm{B}^-$$

The electrolyte and the dissociated ions are in ionic equilibrium. Let C be the initial concentration of the electrolyte in mol L^{-1}. If α is the degree of dissociation, then at equilibrium the concentrations will be:

Species	[AB]	$[\mathrm{A}^+]$	$[\mathrm{B}^-]$
Concentration (mol L^{-1})	$C(1-\alpha)$	$C\alpha$	$C\alpha$

Rate of dissociation (forward reaction) = $k_1C(1-\alpha)$
Rate of combination (backward reaction) = $k_2C\alpha \times C\alpha$

Since ionic equilibrium is a special case of chemical equilibrium, the law of mass action can also be applied to it. So from law of mass action, the rate of dissociation and combination at equilibrium can be equated as:

$$k_1C(1-\alpha) = k_2C\alpha \times C\alpha$$

$$\frac{C\alpha \times C\alpha}{C(1-\alpha)} = \frac{k_1}{k_2} = K_C$$

$$K_C = \frac{\alpha^2 C}{1-\alpha} \text{mol L}^{-1} \tag{10.1}$$

where K_C is the dissociation or ionization constant. Consider one mole of an electrolyte dissolved in volume V of solution, then

$$C = \frac{1}{V}$$

where V is known as the dilution for the solution. Substituting in Eq. (9.1), we get

$$K_C = \frac{\alpha^2}{(1-\alpha)V} \tag{10.2}$$

This expression, correlates the variation of the degree of dissociation of an electrolyte with dilution is known as **Ostwald's dilution law**. Let us consider the application of this law to weak and strong electrolytes. In weak electrolytes, the degree of dissociation is small, that is, $\alpha \ll 1$, therefore, $1 - \alpha \approx 1$. Thus, the expression for Ostwald's dilution law reduces to

$$K_C = \frac{\alpha^2}{V}$$

or
$$\alpha = \sqrt{K_C V} = \sqrt{\frac{K_C}{C}}$$

$$\alpha = K'\sqrt{V} = K'\sqrt{\frac{1}{C}}$$

where $K' = \sqrt{K}$. Thus for a weak electrolyte, the degree of dissociation is inversely proportional to square root of concentration. In strong electrolytes, α is large and cannot be neglected in comparison to 1. Thus,

$$K_C = \frac{\alpha^2}{(1-\alpha)V}$$

or
$$\alpha^2 = K_C V - K_C \alpha V$$

or
$$\alpha^2 + \alpha K_C V - K_C V = 0$$

Solution of this quadratic equation gives the value of α.

Limitations of Ostwald's Law

The law holds good only for weak electrolytes but fails for strong electrolytes due to following factors:

1. The law is based on the fact that the electrolyte is partly ionized at ordinary dilution and completely ionized at infinite dilution. This is true only for weak electrolytes as strong electrolytes are completely ionized at all dilutions.
2. When the concentrations of ions are high, the chemical equilibrium is affected by the presence of these ions and the law of mass action does not hold in its simple form.

Solved Example 10-1

At 25°C the dissociation constant of HCN is 4.9×10^{-10} M. Calculate the degree of dissociation of HCN if the concentrations are **(a)** 0.1 M and **(b)** 0.01 M.

Solution

The reaction can be represented as

$$\begin{array}{cccc} \text{HCN} + \text{H}_2\text{O} & \rightleftharpoons & \text{H}_3\text{O}^+ & + \text{CN}^- \\ C & & 0 & 0 \\ C(1-\alpha) & & \alpha C & \alpha C \end{array}$$

Therefore, $K_C = \dfrac{C\alpha^2}{1-\alpha}$; $1-\alpha \simeq 1$; $\alpha = \sqrt{\dfrac{K_C}{C}}$

(a) $\alpha = \sqrt{\dfrac{4.9\times 10^{-10}}{0.1}} = 7\times 10^{-5}$

(b) $\alpha = \sqrt{\dfrac{4.9\times 10^{-10}}{0.01}} = 2.21\times 10^{-4}$

Common Ion Effect

Let us consider the ionization of a weak binary electrolyte AB

$$\text{AB} \rightleftharpoons \text{A}^+ + \text{B}^-$$

Applying law of mass action, the ionization constant is given by

$$K = \frac{[\text{A}^+][\text{B}^-]}{[\text{AB}]}$$

When another electrolyte that is capable of furnishing either A^+ or B^- ions is added to the solution, the concentration of that ion increases in the solution. For the value of equilibrium constant to remain constant, the equilibrium shifts in the direction of backward reaction in accordance with Le Chatelier's principle. As a result the extent of dissociation of electrolyte is suppressed. This effect is termed as common ion effect and is defined as the suppression in degree of dissociation of an electrolyte by addition of an electrolyte containing a common ion. For example, the dissociation of acetic acid in solution is suppressed if a strong acid (with H^+ as common ion) or salt of a strong base such as sodium acetate (with acetate ion as common ion) is added. Because of the suppressed dissociation, the concentration of the ion that is not in common with added electrolyte decreases.

For mathematical explanation of common ion effect, consider the following cases:

Case 1: Consider the weak acid CH_3COOH with degree of dissociation α_1. Then

$$\begin{array}{lcccc} & \text{CH}_3\text{COOH} & \rightleftharpoons & \text{CH}_3\text{COO}^- & + \text{H}^+ \\ \text{At } t=0 & C_1 & & 0 & 0 \\ \text{At } t=t_{\text{eq}} & C_1(1-\alpha_1) & & C_1\alpha_1 & C_1\alpha_1 \end{array}$$

Therefore,

$$K = \frac{(C_1\alpha_1)(C_1\alpha_1)}{C_1(1-\alpha_1)}$$

Since $\alpha_1 \ll 1$, therefore $(1 - \alpha_1) \approx 1$. Therefore,

$$\alpha_1 = \sqrt{\frac{K}{C}}$$

Case 2: Consider the weak acid CH_3COOH in presence of strong acid HCl with degree of dissociation α_2.

$$\begin{array}{lcccc} & \text{CH}_3\text{COOH} & \rightleftharpoons & \text{CH}_3\text{COO}^- & + \text{H}^+ \\ \text{At } t=0 & C_1 & & 0 & 0 \\ \text{At } t=t_{\text{eq}} & C_1(1-\alpha_2) & & C_1\alpha_2 & C_1\alpha_2 + C_2 \end{array}$$

Similarly,

$$\begin{array}{lccccc} & \text{HCl} & \rightleftharpoons & \text{H}^+ & + & \text{Cl}^- \\ \text{At } t=0 & C_2 & & 0 & & 0 \\ \text{At } t=t_{\text{eq}} & 0 & & C_1\alpha_2 + C_2 & & C_2 \end{array}$$

Then using simultaneous equilibrium concept

$$K = \frac{(C_1\alpha_2)(C_1\alpha_2 + C_2)}{C_1(1-\alpha_2)}$$

Since $\alpha_2 \ll 1$, therefore $(1 - \alpha_2) \approx 1$. Therefore,

$$K = \frac{(C_1\alpha_2)(C_1\alpha_2 + C_2)}{C_1} = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

In the above expression, K and CH_3COOH are constant, therefore, the product

$$[H^+][CH_3COOH] = \text{constant}$$

Also, $[H^+]$ has increased due to the presence of common ion, therefore, $C_1\alpha_2$ must decrease or α_2 must decrease. So, $\alpha_2 < \alpha_1$.

Solved Example 10-2

Acetic acid is less acidic in sodium acetate solution than sodium chloride solution. Give reason.

Solution

This is because of common ion effect of CH_3COO^- ions that suppress the ionization of acetic acid, thus making it less acidic.

Solved Example 10-3

The following equilibrium exists in aqueous solution $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$. If dil. HCl is added without change in temperature, the concentration of CH_3COO^- will decrease. Why?

Solution

If dil. HCl is added to the above equilibrium reaction, the concentration of CH_3COO^- will decrease due to the common ion effect, that is, suppression in the degree of dissociation of a weak electrolyte by adding a strong electrolyte containing a common ion. Here, HCl is a strong electrolyte, when it is added it splits into H^+ and Cl^- ion. As a result, H^+ is the common ion in the equilibrium and hence the concentration of CH_3COO^- decreases.

10.3 | CONCEPTS OF ACIDS AND BASES

Acids and bases constitute a class of compounds that include some of our most familiar chemicals vinegar, lemon juice, liquid in automobile batteries and important laboratory reagents. Some general properties common to aqueous solutions of acids and bases are as follows. Acids generally have a tart (sour) taste, whereas **bases** have a somewhat bitter taste and have a soapy "feel". Acids and bases also affect the colors of certain dyes we call **acid–base indicators**. An example is litmus which has a pink or red color in an acidic solution and a blue color in a basic solution.

Arrhenius Concept

In 1884, a Swedish chemist, Svante Arrhenius, suggested that the particular composition of these compounds determined their behavior. According to him,

1. Acids are compounds that produce H^+ ions in water. For example,

$$HCl + H_2O \rightarrow H_3O^+(aq) + Cl^-(aq)$$

Instead of H^+, the acid species known as the **hydronium ion** (H_3O^+) is used, which is H^+ ion in a hydrated form. In fact, the nature of H^+ in aqueous solution is even more complex than H_3O^+ (i.e., $H_5O_2^+$, $H_7O_3^+$, etc.). The acid species can be represented as H^+(aq) or H_3O^+(aq), depending on the convenience of the particular situation.

2. Bases are compounds that produce OH^- ions in water forming basic solutions (or alkaline/caustic solutions). For example, sodium hydroxide (also known as caustic soda), potassium hydroxide (caustic potash), calcium hydroxide (slaked lime) and ammonia. Except for ammonia, these compounds are all solid ionic compounds.

$$NaOH(s) \xrightarrow{H_2O} Na^+(aq) + OH^-(aq)$$
$$Ba(OH)_2(s) \xrightarrow{H_2O} Ba^{2+}(aq) + 2OH^-(aq)$$

Limitations

1. The conceptual definitions of acids and bases proposed by Arrhenius are applicable only to aqueous solutions.
2. It cannot account for the basic nature of substances that do not contain a hydroxyl group or for the acidic nature of substances that do not contain a hydrogen (hydronium) ion.

Brönsted–Lowry Concept

Johannes Brönsted (1879–1947), a Danish chemist, and Thomas Lowry (1874–1936), a British scientist, realized that the important features in most acid–base reactions is the transfer of a proton from one species to another. According to them,

1. Acids are species that donate protons. For example, hydrogen chloride is an acid because when it reacts with ammonia, HCl molecules donate protons to NH_3 molecules.
2. Bases are species that accept protons. For example, ammonia is a base because NH_3 molecules accept protons.

This suggests that acid–base reactions are proton transfer reactions.

$$NH_3(aq) + HCl(l) \rightleftharpoons NH_4^+(aq) + Cl^-(aq)$$

Note: Even when water is the solvent, Brönsted–Lowry definitions are used in preference to Arrhenius definitions. Thus, the reaction between HCl and water is clearly a Brönsted–Lowry acid–base reaction.

In this concept, an acid–base reaction is considered to be in chemical equilibrium, having both forward and reverse reactions. For example, the ionization of weak acid like formic acid is slow and is in chemical equilibrium with water acting as both solvent and reactant. This equilibrium is a typical proton transfer equilibrium.

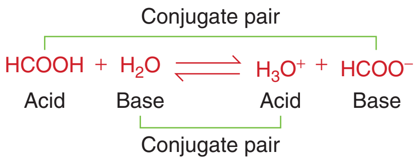
$$HCOOH(aq) + H_2O \rightleftharpoons H_3O^+(aq) + HCOO^-(aq)$$

In the forward reaction, HCOOH behaves as a **Brönsted acid**, a **proton donor** and water behaves as a **Brönsted base**, a **proton acceptor**. In the reverse reaction, H_3O^+ behaves as a Brönsted acid, while $HCOO^-$ ion behaves as a Brönsted base.

Conjugate Acid–Base Pairs

Two substances that differ from each other only by one proton are referred to as a **conjugate acid–base pair**. Thus, H_3O^+ and H_2O are such a pair with H_3O^+ having one more proton than H_2O. In the pair, the **conjugate acid** is the proton donor and the **conjugate base** is the pair's proton acceptor. Thus, H_3O^+ is the conjugate acid of H_2O, and H_2O is the conjugate base of H_3O^+.

In any Brönsted–Lowry acid–base equilibrium, there are invariably *two* conjugate acid–base pairs. These are represented by connecting them with a line as shown:



It can be seen from the diagram that in the aqueous formic acid equilibrium, the pair HCOOH and $HCOO^-$ is one conjugate acid–base pair and H_2O and H_3O^+ is the other.

Amphoteric Substances

A substance that can be either an acid or a base depending on the other substance present is said to be **amphoteric** (Greek *amphoteros*, "partly one and partly the other"). Another term is **amphiprotic** to stress that the *proton* donating or accepting ability is of central concern.

Amphoteric or amphiprotic substances may be either molecules or ions. For example, anions of acid salts, such as the bicarbonate ion of baking soda, are amphoteric. The HCO_3^- ion can either donate a proton to a base or accept a proton from an acid. Thus towards the hydroxide ion, the bicarbonate ion is an acid; it donates its proton to OH^-.

$$\underset{\text{Acid}}{HCO_3^-(aq)} + \underset{\text{Base}}{OH^-(aq)} \rightarrow CO_3^{2-}(aq) + H_2O(aq)$$

Towards hydronium ion, however, HCO_3^- is a base; it accepts a proton from H_3O^+.

$$\underset{\text{Base}}{HCO_3^-(aq)} + \underset{\text{Acid}}{H_3O^+(aq)} \rightarrow H_2CO_3(aq) + H_2O(aq)$$

Limitation: There are some reactions which do not involve proton transfer and have properties similar to acid–base reactions. For example, if gaseous SO_3 is passed over solid CaO, a reaction occurs in which $CaSO_4$ forms.

$$CaO(s) + SO_3(g) \rightarrow CaSO_4(s)$$

If these reactants are dissolved in water first, they react to form $Ca(OH)_2$ and H_2SO_4, and when their solutions are mixed the following reaction takes place:

$$Ca(OH)_2(aq) + H_2SO_4(aq) \rightarrow CaSO_4(s) + 2H_2O$$

The same two initial reactants, CaO and SO_3, form the same ultimate product, $CaSO_4$. However, there are no protons being transferred. Thus, further generalizations were required for acid–base concept.

Leveling Effect

All the bronsted acids, which are stronger than $[H_3O]^+$ or $[H]^+$ will essentially be completely ionized in aqueous solution. For example,

$$HNO_3 + H_2O \rightleftharpoons H_3O^+ + NO_3^-$$

$$HBr + H_2O \rightleftharpoons H_3O^+ + Br^-$$

Thus, in the above case both HNO_3 and HBr will have the same acidic strength in aq. solution (assuming they have the same concentration).

We can therefore say that all acids which are stronger than H^+ or H_3O^+ will have same acid strength, if they have the same concentration.

Water is said to have a leveling effect on acids stronger than H_3O^+. In other words, the strongest acid that can exist in aqueous solutions is the conjugate acid of H_2O or H_3O^+ ion. Acids weaker than H_3O^+ will not be leveled by H_2O and will have different degree of ionization. For example, H_3PO_4, H_2S, etc. Similarly, Brönsted bases stronger than OH^- are levelled by H_2O. For example, H^- and NH_2^- have the same basic strength in aqueous solution. Both H^- and NH_2^- are stronger than OH^-. They are leveled by H_2O.

$$H^- + H_2O \rightleftharpoons H_2 + OH^-$$

$$NH_2^- + H_2O \rightleftharpoons NH_3 + OH^-$$

Leveling effect can also be observed for solvents other than H_2O. For example, if liq. NH_3 is the solvent, all acids which are stronger than conjugate acid of NH_3 (the strongest acid that can exist in liq. NH_3) will levelled by NH_3. Similarly, all bases which are stronger than conjugate base of NH_3 (the strongest base that can exist in liq. NH_3) will leveled by NH_3.

Solved Example 10-4

Arrange the following oxides in the increasing order of Brönsted basicity. **(IIT-JEE 2004)**

$$Cl_2O_7, BaO, SO_3, CO_2, B_2O_3$$

Solution

$BaO + H_2O \rightleftharpoons Ba(OH)_2$ (basic)

$CO_2 + H_2O \rightleftharpoons H_2CO_3$ (weakly acidic)

$SO_3 + H_2O \rightleftharpoons H_2SO_4$ (strongly acidic)

$B_2O_3 + 3H_2O \rightleftharpoons 2H_3BO_3$ (very weakly acidic)

$Cl_2O_7 + H_2O \rightleftharpoons 2HClO_4$ (very strongly acidic)

Hence, the order is $Cl_2O_7 < SO_3 < CO_2 < B_2O_3 < BaO$.

Solved Example 10-5

(a) What is the conjugate base of nitric acid, HNO_3, and what is the conjugate acid of the hydrogen sulphate ion, HSO_4^-?

(b) Write the formula of the conjugate acid for each of the following Brönsted bases: (i) HO_2^-, (ii) SO_4^{2-}, (iii) CO_3^{2-}, (iv) CN^-, (v) NH_2^- and (vi) NH_3.

Solution

(a) Removing one H^+ (both the atom and the charge) from HNO_3 leaves NO_3^-. The nitrate ion, NO_3^-, is thus the conjugate base of HNO_3. Adding an H^+ to HSO_4^- gives its conjugate acid, H_2SO_4.

(b) (i) H_2O_2, (ii) HSO_4^-, (iii) HCO_3^-, (iv) HCN, (v) NH_3 (vi) NH_4^+.

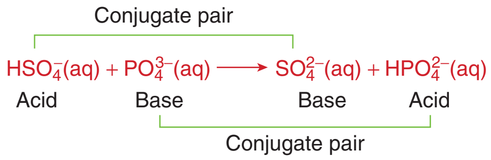
Solved Example 10-6

The anion of sodium hydrogen sulphate, HSO_4^-, reacts as follows with the phosphate ion, PO_4^{3-}. Identify the two conjugate acid–base pairs.

$$HSO_4^-(aq) + PO_4^{3-}(aq) \rightarrow SO_4^{2-}(aq) + HPO_4^{2-}(aq)$$

Solution

There are two ions in the equilibrium that contain "PO_4", so they must belong to the same conjugate pair. The one with the greater number of hydrogens, HPO_4^{2-}, must be the Brönsted acid, and the other, PO_4^{3-}, must be the Brönsted base. Therefore, one conjugate acid–base pair is HPO_4^{2-} and PO_4^{3-}. The other two ions, HSO_4^- and SO_4^{2-}, belong to the second conjugate acid–base pair; HSO_4^- is the conjugate acid and SO_4^{2-} is the conjugate base.



Solved Example 10-7

Which of the following are conjugate acid–base pairs? Describe why the others are not true conjugate acid–base pairs. **(a)** H_3PO_4 and $H_2PO_4^-$, **(b)** HI and H^+, **(c)** NH_2^- and NH_3, **(d)** HNO_2 and NH_4^+, **(e)** CO_3^{2-} and CN^-, **(f)** HPO_4^{2-} and $H_2PO_4^-$.

Solution

Conjugate acid–base pairs are (a), (c) and (f).

(b) The conjugate base of HI is I^-.

(d) The conjugate base of HNO_2 is NO_2^- and the conjugate base of NH_4^+ is NH_3.

(e) The conjugate acid of CO_3^{2-} is HCO_3^- and the conjugate acid of CN^- is HCN.

Solved Example 10-8

Write the formula of the conjugate base for each of the following Brönsted acids: **(a)** H_2O, **(b)** HI, **(c)** HNO_2, **(d)** H_3PO_4, **(e)** $H_2PO_4^-$, **(f)** HPO_4^{2-}, **(g)** H_2S and **(h)** NH_4^+.

Solution

In each case the conjugate base is obtained by removing a proton from the acid:

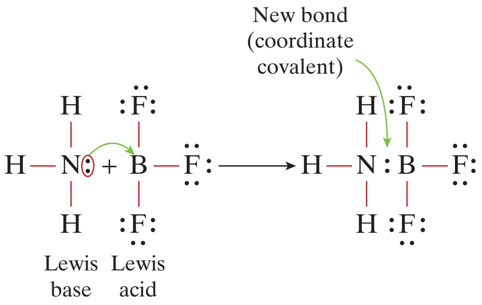
(a) OH^- **(b)** I^- **(c)** NO_2^- **(d)** $H_2PO_4^-$

(e) HPO_4^{2-} **(f)** PO_4^{3-} **(g)** HS^- **(h)** NH_3

Lewis Concept of Acids and Bases

G.N. Lewis, after whom Lewis symbols are named, provided further generalizations as follows:

1. **Lewis acid** is any ionic or molecular species that can accept a pair of electrons in the formation of a coordinate covalent bond. These substances have an incomplete valence shell, such as BF_3 or H^+.
2. **Lewis base** is any ionic or molecular species that can donate a pair of electrons in the formation of a coordinate covalent bond. These substances have completed valence shells and unshared pairs of electrons, such as NH_3, H_2O, and O^{2-}.

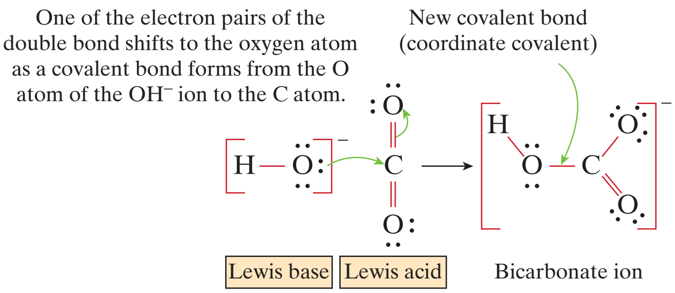


Consider the reaction between BF_3 and NH_3. The reaction is exothermic because a bond is formed between N and B, with the nitrogen donating an electron pair and the boron accepting it. It illustrates a Lewis acid–base neutralization and can be represented using Lewis representation as shown:

The ammonia molecule acts as a Lewis base. The boron atom in BF_3, having only six electrons in its valence shell and needing two more to achieve an octet, accepts the pair of electrons from the ammonia molecule. Hence, BF_3 is functioning as a Lewis acid.

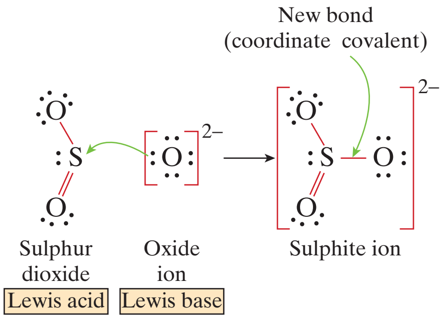
The types of substances that can act as Lewis acids and bases are listed as follows:

1. **Lewis acids:**
   - **(a)** Molecules with incomplete valence shells octets (e.g., BF_3, $AlCl_3$, BCl_3, etc).
   - **(b)** Positively charged species or cations such as H^+ or Ag^+. All cations can be expected to act as Lewis acids because they are electron deficient. However, for most of the cations such as K^+, Na^+, Ca^{2+}, the tendency to accept electrons is low, so only H^+ or Ag^+ act as Lewis acids.
   - **(c)** Molecules or ions with complete valence shells, but with multiple bonds that can be shifted to make room for more electrons. These are generally molecules having a multiple bond between atoms of dissimilar electronegatively (e.g., CO_2, SO_2, SO_3).


One of the electron pairs of the double bond shifts to the oxygen atom as a covalent bond forms from the O atom of the OH^- ion to the C atom.

New covalent bond (coordinate covalent)

   - **(d)** Molecules or ions that have central atoms capable of holding additional electrons (usually, atoms of elements in the third period and below) (e.g., SO_2).



(e) Molecules in which the central atom has empty *d*-orbitals and can therefore accept an electron pair and act as Lewis acids. For example, halides such as GeX_4, SiX_4, SnX_4, PX_3, etc., (where X = –Cl, –Br, –I).

2. Lewis bases: Molecules or ions that have unshared pairs of electrons and that have complete valence shells (e.g., O^{2-}, NH_3).

These are of two types:

(a) Neutral species having at least one lone pair of electrons, such as ammonia, amines, alcohols, etc.

(b) Negatively charged species or anions, such as chloride, cyanide, hydroxide, ions, etc.

> **Note:** We can see that Lewis theory applies well to explain both Arrhenius and Brönsted–Lowry definitions of acids and bases. The Arrhenius theory is the most limited in its definition for acid and bases, whereas Brönsted–Lowry theory can account for Arrhenius concept of acid and bases. For aqueous solutions, generally the Brönsted–Lowry definition of acids and bases is considered.

Limitations: This concept fails to explain the behavior of monoprotic and polyprotic acids, such as HCl, H_2SO_4, etc., that do not accept an electron pair and do not undergo coordination bonding. Further, it does not help in predicting the relative strength of acids and bases. It does not explain catalytic activity of Lewis acids (e.g., Ziegler-Natta catalyst), and the slow coordination reactions as opposed to fast acid-base neutralization reactions.

Solved Example 10-9

Predict if each of the following will behave as a Lewis acid or a Lewis base. Give reasons for your answer,

(a) Fluoride ion **(b)** $BeCl_2$ molecule

(c) ISO_3

Solution

(a) Fluoride ions have a filled octet of electrons and are likely to behave as Lewis bases, that is, electron pair donors.

(b) $BeCl_2$ is a likely Lewis acid since it has an incomplete shell. The Be atom has only two valence electrons and it can easily accept a pair of electrons.

(c) SO_3 could be considered as a potential Lewis base since it contains three oxygen atoms, each with lone pairs and partial negative charges. However, it is more effective as a Lewis acid, since the central sulphur atom bears a significant positive charge.

Solved Example 10-10

Identify the Lewis acids and bases in each aqueous reaction.

(a) $NH_3 + H^+ \rightleftharpoons NH_4^+$

(b) $(CH_3)_2O + BCl_3 \rightleftharpoons (CH_3)_2OBCl_3$

(c) $Ag^+ + 2NH_3 \rightleftharpoons Ag(NH_3)_2^+$

Solution

(a) NH_3 is the Lewis base since it has an unshared pair of electrons. H^+ is the Lewis acid since it can accept a pair of electrons.

(b) $(CH_3)_2O$ is the Lewis base and BCl_3 is the Lewis acid.

(c) Ag^+ is the Lewis acid and NH_3 is the Lewis base.

10.4 | ACID–BASE EQUILIBRIA AND IONIZATION CONSTANTS

Ionization of acids and bases generally occurs in aqueous medium in chemical and biological systems. The strong acids and bases are considered to be 100% dissociated in an aqueous solution. This makes calculating the concentrations of H_3O^+ and OH^- in their solutions a relatively simple task. Weak acids and bases are incompletely ionized in water and exist in solution as molecules that are in equilibria with the ions formed by their reactions with water.

Another term called **percentage ionization** of the acid or base, is defined as follows:

$$\text{Percentage ionization} = \frac{\text{Moles ionized per liter}}{\text{Moles available per liter}} \times 100\% \qquad (10.3)$$

We will discuss the determination of their ionization constants in the following sections.

Ionization Constants of Weak Acids

The weak acids and bases are incompletely ionized in water and exist in solution as molecules that are in equilibria with the ions formed by their reactions with water.

$$HA + H_2O \rightleftharpoons H_3O^+ + A^- \qquad (10.4)$$

where HA is any acid. A general equation for the equilibrium law using K_C' to stand for the equilibrium constant can be written as:

$$K_C' = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

Since in dilute aqueous solutions $[H_2O]$ can be considered a constant, so it can be combined with K_C' to give a new equilibrium constant.

$$K_C' \times [H_2O] = \frac{[H_3O^+][A^-]}{[HA]} = K_a$$

or

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

This new constant K_a is called an **acid dissociation or ionization constant**. The equilibrium concentrations can be calculated as follows:

The undissociated acid and the dissociated ions are in ionic equilibrium. Let C be the initial concentration of the acid in mol L^{-1}. If α is the **degree of dissociation**, then at equilibrium the concentrations will be

$$\underset{C(1-\alpha)}{HA(aq)} + H_2O(l) \rightleftharpoons \underset{C\alpha}{A^-} + \underset{C\alpha}{H_3O^+}$$

Rate of dissociation (forward reaction) = $k_1 C(1-\alpha)$
Rate of combination (backward reaction) = $k_2 (C\alpha)(C\alpha)$

Using the law of chemical equilibrium, the rate of dissociation and combination of ions at equilibrium can be equated:

$$k_1 C(1-\alpha) = k_2 (C\alpha)(C\alpha)$$

$$\frac{(C\alpha)\,(C\alpha)}{C(1-\alpha)} = \frac{k_1}{k_2} = K_\mathrm{a}$$

$$K_\mathrm{a} = \frac{\alpha^2 C}{1-\alpha}\ \mathrm{mol\ L^{-1}} \tag{10.5}$$

where K_a is the dissociation or ionization constant of acid. For weak acids, values of K_a are usually quite small and can be conveniently represented in a logarithmic form. Thus, we can define the pK_a of an acid as

$$\mathrm{p}K_\mathrm{a} = -\log K_\mathrm{a}$$

Also, K_a = antilog(−pK_a) or $K_\mathrm{a} = 10^{-\mathrm{p}K_\mathrm{a}}$. The strength of a weak acid is determined by its value of K_a. The larger the value of K_a, the stronger and more fully ionized is the acid. Because of the negative sign in the defining equation for pK_a, the *stronger* the acid, the *smaller* is its value of pK_a. The values of K_a and pK_a for some typical weak acids are given in Table 10.1. The values of K_a for strong acids are very large and are not tabulated. For many strong acids, K_a values have not been measured.

Table 10.1 K_a and pK_a values for weak monoprotic acids at 25°C

Name of Acid	Formula	K_a	pK_a
Iodic acid	HIO_3	1.7×10^{-1}	0.77
Chloroacetic acid	$ClCH_2COOH$	1.36×10^{-3}	2.87
Nitrous acid	HNO_2	7.1×10^{-4}	3.15
Hydrofluoric acid	HF	6.8×10^{-4}	3.17
Cyanic acid	HOCN	3.5×10^{-4}	3.46
Formic acid	$HCHO_2$	1.8×10^{-4}	3.74
Barbituric acid	$HC_4H_3N_2O_3$	9.8×10^{-5}	4.01
Acetic acid	CH_3COOH	1.8×10^{-5}	4.74
Hydrazoic acid	HN_3	1.8×10^{-5}	4.74
Butanoic acid	$CH_3CH_2CH_2COOH$	1.52×10^{-5}	4.82
Propanoic acid	CH_3CH_2COOH	1.34×10^{-5}	4.87
Hypochlorous acid	HOCl	3.0×10^{-8}	7.52
Hydrocyanic acid (aq)	HCN	6.2×10^{-10}	9.21
Phenol	C_6H_5OH	1.3×10^{-10}	9.89
Hydrogen peroxide	H_2O_2	1.8×10^{-12}	11.74

Ionization Constants of Weak Bases

The weak Brönsted bases and are proton acceptors. Examples are ammonia, NH_3 and acetate ion, CH_3COO^-. Their reactions with water are

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$
$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

Notice that, in each instance, the base reacts with water to give OH^- and the corresponding conjugate acid. We can also represent these reactions by a general equation. If we represent the base by the symbol B, the reaction is

$$\underset{C(1-\alpha)}{\mathrm{B}} + H_2O \rightleftharpoons \underset{C\alpha}{BH^+} + \underset{C\alpha}{OH^-}$$

(As with weak acids, B does not have to be electrically neutral.) This yields the equilibrium law

$$K_C' = \frac{[\mathrm{BH^+}][\mathrm{OH^-}]}{[\mathrm{B}][\mathrm{H_2O}]}$$

As with solutions of weak acids, the quantity $[H_2O]$ in the denominator is effectively a constant that can be combined with K_C' to give a new constant that we call the **base dissociation or ionization constant**, K_b.

$$K_\mathrm{b} = \frac{[\mathrm{BH^+}][\mathrm{OH^-}]}{[\mathrm{B}]} = \frac{(C\alpha)^2}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha} \tag{10.6}$$

Because the K_b values for weak bases are usually small numbers, the same kind of logarithmic notation is often used to represent their equilibrium constants. Thus, pK_b is defined as

$$\mathrm{p}K_\mathrm{b} = -\log K_\mathrm{b}$$

Also, $K_b = \text{antilog}(-pK_b)$ or $K_b = 10^{-pK_b}$. We know that ammonia acts as a base in aqueous solutions, yielding OH^- ions.

$$\mathrm{NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)}$$

Amines are organic compounds that can be considered as derivatives of ammonia, in which one or more hydrogen atoms of ammonia are replaced by another group. These also behave as weak bases. Table 10.2 lists some weak molecular bases and their corresponding values of K_b and pK_b.

Table 10.2 K_b and pK_b values for weak molecular bases at 25°C

Name of Base	Formula	K_b	pK_b
Butylamine	$C_4H_9NH_2$	5.9×10^{-4}	3.23
Methylamine	CH_3NH_2	4.4×10^{-4}	3.36
Ammonia	NH_3	1.8×10^{-5}	4.74
Strychnine	$C_{21}H_{22}N_2O_2$	1.0×10^{-6}	6.00
Hydrazine	N_2H_4	9.6×10^{-7}	6.02
Morphine	$C_{17}H_{19}NO_3$	7.5×10^{-7}	6.13
Hydroxylamine	$HONH_2$	6.6×10^{-9}	8.18
Pyridine	C_5H_5N	1.5×10^{-9}	8.82
Aniline	$C_6H_5NH_2$	4.1×10^{-10}	9.39

Note: For strong acids and strong base, K_a or K_b will tend towards infinity (∞) or will be very large (because $\alpha \cong 1$).

Ionic Product of Water

The ionization of water takes place in all aqueous solutions, this knowledge gives us an insight into the acid–base equilibria. Pure water has been found to weakly conduct electricity, indicating the presence of very small concentrations of ions arising from the very slight self-ionization, or *autoionization*, of water itself.

$$\underset{\text{Acid}}{\mathrm{H_2O(l)}} + \underset{\text{Base}}{\mathrm{H_2O(l)}} \rightleftharpoons \underset{\text{Conjugate acid}}{\mathrm{H_3O^+(aq)}} + \underset{\text{Conjugate base}}{\mathrm{OH^-(aq)}}$$

or,

$$\mathrm{H_2O \rightleftharpoons H^+ + OH^-}$$

Its equilibrium law is

$$K_\mathrm{C} = \frac{[\mathrm{H^+}][\mathrm{OH^-}]}{[\mathrm{H_2O}]}$$

In pure water, and even in dilute aqueous solutions, the molar concentration of water is essentially a constant, with a value of (1000 g L^{-1})/(18 g mol^{-1}) = 55.55 mol L^{-1}. Therefore,

$$K_C \times [H_2O] = [H^+][OH^-]$$

The product of the two constants, $K_C \times [H_2O]$, must also be a constant. Because of the importance of the ionization equilibrium, it is given the special symbol K_w and is called the **ionic product or ionization constant of water**.

$$K_w = [H^+][OH^-]$$

In pure water, the concentrations of H^+ and OH^- produced by the autoionization are equal because the ions are formed in equal numbers. It has been found that the concentrations have the following values at 25°C.

$$[H^+] = [OH^-] = 1.0 \times 10^{-7} \text{ mol L}^{-1}$$

Therefore, at 25°C, $K_w = (1.0 \times 10^{-7}) \times (1.0 \times 10^{-7}) = 1.0 \times 10^{-14}$ (at 25°C). The value of equilibrium constant for dissociation of H_2O to give H^+ and OH^- is given by

$$\frac{10^{-7}}{55.55} = 1.8 \times 10^{-9}$$

So the equilibrium of autoionization lies mainly towards undissociated water molecules. As with other equilibrium constants, the value of K_w varies with temperature (Table 10.3).

Table 10.3 K_w at various temperatures

Temperature (°C)	0	10	20	25	30	37	40	50	60
K_w	1.5×10^{-15}	3.0×10^{-15}	6.8×10^{-15}	1.0×10^{-14}	1.5×10^{-14}	2.5×10^{-14}	3.0×10^{-14}	5.5×10^{-14}	9.5×10^{-14}

Because of the autoionization of water, there are always both H^+ and OH^- ions in any aqueous solution, regardless of what solutes are present. This means that in a solution of the acid, HCl, there is some OH^-, and in a solution of the base, NaOH, there is some H_3O^+. Bases on their molar concentrations, we find that

1. A **neutral solution** is one in which $[H^+] = [OH^-]$; neither ion is present in a greater concentration than the other.
2. An **acidic solution** is one in which $[H^+] > [OH^-]$, that is, some solute has made the molar concentration of H^+ greater than that of OH^-.
3. A **basic solution** exists when $[H^+] < [OH^-]$, that is, the molar concentration of OH^- exceeds that of H^+.

Solved Example 10-11

An aqueous solution of sodium bicarbonate, $NaHCO_3$, has a molar concentration of hydroxide ion of 7.8×10^{-6} M. What is the molar concentration of hydrogen ion? Is the solution acidic, basic or neutral?

Solution

We know that $K_w = 1.0 \times 10^{-14} = [H^+][OH^-]$. Now,

$$[H^+] = \frac{1.0 \times 10^{-14}}{[OH^-]} = \frac{1.0 \times 10^{-14}}{7.8 \times 10^{-6}} = 1.3 \times 10^{-9} \text{ M}$$

Since $[OH^-] > [H^+]$, the solution is basic.

pH Concept

With smaller molar concentrations of H^+ and OH^- in solutions of weak acids and bases, we come across negative exponents while comparing their values. S.P.L. Sörenson (1868–1939) suggested an easier approach involving only one number called the **pH** of the solution. It is the negative logarithm to base 10 of the activity (a_{H^+}) of hydrogen ion. Activity can be defined in terms of molar concentrations as

$$a_{H^+} = \frac{[H^+]}{\text{mol L}^{-1}}$$

In dilute solutions (<0.01 mol), the activity of hydrogen ion is equal in magnitude to molarity represented by $[H^+]$. By definition, the pH can be written as

$$\text{pH} = -\log a_{H^+} = -\log \frac{[H^+]}{\text{mol L}^{-1}} \qquad (10.7)$$

For dilute solutions, $\text{pH} = -\log[H^+] \Rightarrow [H^+] = 10^{-\text{pH}} = \text{antilog(pH)}$

Note: The logarithmic definition of pH has been adapted to quantities other than $[H^+]$. Thus, for any quantity X, we may define a term, pX, in the following way.

$$\text{pX} = -\log \text{X}$$

To express small concentrations of hydroxide ion, the pOH of a solution can be defined as

$$\text{pOH} = -\log[\text{OH}^-]$$

Similarly, for K_w, we can define $\text{p}K_w$ as follows.

$$\text{p}K_w = -\log K_w$$

The numerical value of $\text{p}K_w$ at 25°C equals $-\log(1.0 \times 10^{-14})$ or $-(-14.00)$. Thus,

$$\text{p}K_w = 14.00 \text{ (at 25°C)}$$

A useful relationship among pH, pOH and $\text{p}K_w$ can be derived that defines K_w.

$$\text{pH} = -\log[H^+], \quad \text{pOH} = -\log[\text{OH}^-]$$

Therefore, $$-\log K_w = -\log[H^+] - \log[\text{OH}^-]$$

$$\text{p}K_w = \text{pH} + \text{pOH}$$

At 25°C $$14 = \text{pH} + \text{pOH}$$

This tells us that in an aqueous solution of any solute at 25°C, pH + pOH = 14.00.

Note: Neutral pH is 7.00 only for 25°C. At other temperatures, a neutral solution still has $[H^+] = [\text{OH}^-]$, but because K_w changes with temperature, so do the values of $[H^+]$ and $[\text{OH}^-]$. This causes the pH of the neutral solution to differ from 7.00. For example, at normal body temperature (37°C), a neutral solution has $[H^+] = [\text{OH}^-] = 1.6 \times 10^{-7}$, so pH = 6.80.

Application of pH

pH is used to measure the acidity of a solution. Hence, we may define *acidic*, *basic*, and *neutral* in terms of pH values.

1. In pure water, or in any solution that is *neutral*. The pH = 7 for a neutral solution at 25°C.

$$[H^+] = [\text{OH}^-] = 1.0 \times 10^{-7} \text{ M}$$

2. An acidic solution is one in which $[H^+] > 10^{-7}$ M $\Rightarrow$ pH < 7.00. Thus, as a solution's acidity increases, its pH decreases.
3. A basic solution is one in which the value of $[H^+] < 10^{-7}$ M $\Rightarrow$ pH > 7.00. As a solution's acidity decreases, its pH increases.

pH Scale

The pH values for some common substances are given on a **pH scale** in Fig. 10.1. It is important to note that the hydrogen ion concentration changes considerably with a relatively small change in pH. Thus, a change of one pH unit corresponds to a 10-fold change in the hydrogen ion concentration. At pH 6.0 the hydrogen ion concentration is 1×10^{-6} mol L^{-1}. At pH 5.0, it is 1×10^{-5} mol L^{-1}, or 10 times greater. That is a major difference. The pH concept is almost never used with solutions having hydrogen ion concentrations greater than 1 mol as it would lead to negative values of pH. For example, in a solution where the value of $[H^+]$ is 2 mol, the pH, would be –log (2.00) or –0.301. There is nothing wrong with negative pH values, but they offer no advantage over the actual value of $[H^+]$.

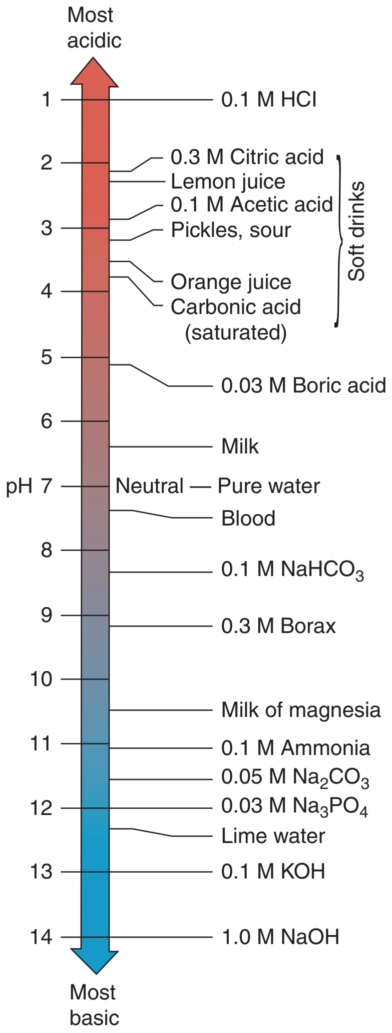


Figure 10.1 The pH scale.

Measuring pH

1. **pH meters:** In pH meter, an electrode system sensitive to the hydrogen ion concentration in a solution is first dipped into a solution of known pH to calibrate the instrument. Once calibrated, the apparatus can then be used to measure the pH of any other solution simply by immersing the electrode into it. Most modern pH meters are able to determine pH values to within ±0.01 pH units, and research-grade instruments are capable of even greater precision in the pH range of 0.0 to 14.0.
2. **pH test papers:** The pH test papers are impregnated with one or more indicator dyes. To obtain a rough idea of the pH, a drop of the solution to be tested is touched to a strip of the test paper and the resulting color is compared with a color code.
3. **Litmus paper:** It is often used qualitatively to test whether a solution is acidic or basic. It consists of porous paper impregnated with litmus dye, made either red or blue by exposure to acid or base, and then dried. Below pH 4.7, litmus is red and above pH 8.3 it is blue. The transition for the color change occurs over a pH range of 4.7 to 8.3 with the center of the change at about 6.5, very nearly a neutral pH. To test whether a solution is acidic, a drop of it is placed on blue litmus paper. If the dye turns pink, the solution is acidic. Similarly, to test if the solution is basic, a drop is placed on red litmus paper. If the dye turns blue, the solution is basic.

Solved Example 10-12

The pH of pure water at 25°C and 35°C are 7 and 6, respectively. Calculate the heat of formation of water from H^+ and OH^-

Solution

At 25°C, $[H^+] = 10^{-7}$ M and $K_w = 10^{-14}$ and at 35°C, $K_w = 10^{-12}$.

Since $$2.303 \log \frac{K_{w_2}}{K_{w_1}} = \frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right[$$

Substituting values, we get

$$2.303 \log \frac{10^{-12}}{10^{-14}} = \frac{\Delta H}{2}\left[\frac{10}{298 \times 308}\right]$$

Solving, we get $\Delta H = 84551.4$ cal mol^{-1} (for dissociation of H_2O) and $K_f(H_2O) = -84.551$ kcal mol^{-1}.

Solved Example 10-13

The K_w for $2H_2O \rightleftharpoons H_3O^+ + OH^-$ changes from 10^{-14} at 25°C to 9.62×10^{-14} at 60°C. What will be the pH and nature of water at 60°C?

Solution

Given that K_w for H_2O at 25°C = 10^{-14}.

$$[H^+]\times[OH^-]=10^{-14}\,(K_w=[H^+][OH^-])$$
$$[H^+]=10^{-7}\,M \Rightarrow pH=7$$

Now, K_w for H_2O at 60°C is $[H^+]=[OH^-]=9.62\times10^{-14}$. For pure water $[H^+]=[OH^-]$

$$[H^+]=9.62\times10^{-14} \text{ and}$$

$$pH=-\log[H^+]=-\log(3.10\times10^{-7})=6.51$$

Thus, pH of water becomes 6.51 at 60°C, but the nature is neutral since calculation for pure water has been made, that is, pH scale at 60°C extends from 0 to 13.02.

Solved Example 10-14

What is the pH of a sodium hydroxide solution at 25°C in which the hydroxide ion concentration equals 0.0026 M?

Solution

There are two ways to solve this problem. We could use the tool concerning the K_w expression ($K_w=[H^+][OH^-]=1\times10^{-14}$) and the given value of the hydroxide ion concentration to find $[H^+]$, and then calculate the pH. The second way would be to use the tool defining pOH to calculate the pOH from the hydroxide ion concentration ($pOH=-\log[OH^-]$) and then subtract the pOH from 14.00 to find the pH. The second path requires less effort, so let us proceed that way.

First, we substitute the $[OH^-]$, which equals 0.0026 M, into the equation for pOH.

$$pOH=-\log[OH^-]=-\log(0.0026)=-\log(-2.59)=2.59$$

Then we subtract this pOH value from 14.00 to find the pH.

$$pOH=14.00-2.59=11.41$$

Notice that the pH in this basic solution is well above 7. The molar concentration of hydroxide ion is between 0.001 (or 10^{-3}) and 0.01 (or 10^{-2}), so the pOH must be between 3 and 2, which it is. Thus, the pH ought to be between 11 and 12.

Solved Example 10-15

Calculate the values of pH, pOH, and $[OH^-]$ for the following solutions: **(a)** 0.020 M HCl, **(b)** 0.00035 M $Ba(OH)_2$, **(c)** 0.01 N H_2SO_4.

Solution

(a) The solute is HCl, which you should recognize as one of the strong acids. Therefore, we expect it to be 100% ionized. From each mole of HCl, we expect one mole of H^+, so we will use the molar concentration of HCl to obtain $[H^+]$, from which we can calculate the pH, pOH, and $[OH^-]$.

In 0.020 M HCl, $[H^+]=0.020$ M. Therefore,

$$pH=-\log(0.020)=1.70$$

Thus in 0.020 M HCl, the pH is 1.70. The pOH is $(14.00-1.70)=12.30$. To find $[OH^-]$, we can use this value of pOH.

$$[OH^-]=10^{-pOH}=10^{-12.30}=5.0\times10^{-13}\,M$$

Notice how much smaller $[OH^-]$ is in this acidic solution than it is in pure water. This makes sense, because the solution is quite acidic.

(b) The solute is $Ba(OH)_2$, is a soluble metal hydroxide, which is also a strong electrolyte. From each mole of $Ba(OH)_2$, there are two moles of OH^- liberated. We will use the molarity of the $Ba(OH)_2$ to calculate the hydroxide ion concentration. From $[OH^-]$, we can calculate pOH and then pH. As noted, for each mole of $Ba(OH)_2$ we obtain two moles of OH^-. Therefore,

$$[OH^-]=2\times0.00035=0.00070\,M$$
$$pH=-\log(0.00070)=3.15$$

Thus, the pOH of this solution is 3.15, and the pH = (14.00 − 3.15) = 10.85. In part (a), the molarity of H^+ is between 0.01 M and 0.1 M, or between 10^{-2} M and 10^{-1} M. So the pH must be between 1 and 2, as we found. In part (b), the molarity of OH^- is between 0.0001 and 0.001, or between 10^{-4} and 10^{-3}. Hence, the pOH must be between 3 and 4, which it is.

(c) The reaction involved is

$$H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{2-}$$

	H_2SO_4	$2H^+$	SO_4^{2-}
Initial moles	10^{-2}	0	0
Moles at equilibrium	0	10^{-2}	10^{-2}

Therefore, $pH=-\log[H^+]=-\log10^{-2}=2$ and $pOH=10$

Deriving Relation between K_a and K_b

Formic acid, HCOOH, is a typical weak acid that ionizes as follows:

$$\text{HCOOH} + \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{HCOO}^-$$

Its K_a expression can be written as:

$$K_a = \frac{[\text{H}^+][\text{HCOO}^-]}{[\text{HCOOH}]}$$

The conjugate base of formic acid is the formate ion, $HCOO^-$, and when a solute that contains this ion (e.g., $NaCHO_2$) is dissolved in water, the solution is slightly basic. In other words, the formate ion is a weak base in water and participates in the equilibrium

$$\text{HCOO}^- + \text{H}_2\text{O} \rightleftharpoons \text{HCOOH} + \text{OH}^-$$

The K_b expression for this base is

$$K_b = \frac{[\text{HCOOH}][\text{OH}^-]}{[\text{HCOO}^-]}$$

There is an important relationship between the equilibrium constants for this acid–base pair. The product of K_a times K_b equals K_w. We can see this by multiplying the mass action expressions.

$$K_a \times K_b = \frac{[\text{H}^+][\text{CHO}_2^-]}{[\text{HCOOH}]} \times \frac{[\text{HCOOH}][\text{OH}^-]}{[\text{CHO}_2^-]} = [\text{H}^+][\text{OH}^-] = K_w$$

In fact, this same relationship exists for *any* acid–base conjugate pair. For *any* acid–base conjugate pair:

$$K_a \times K_b = K_w \tag{10.8}$$

It can also be written as:

$$\text{p}K_a + \text{p}K_b = \text{p}K_w = 14.00 \text{ (at 25°C)} \tag{10.9}$$

Solved Example 10-16

A solution of hydrazine, N_2H_4, has a concentration of 0.25 M. What is the pH of the solution, and what is the percentage ionization of the hydrazine? (K_b of hydrazine $= 9.6 \times 10^{-7}$.)

Solution

Since hydrazine is the only solute in the solution, we will have to write the equation for the ionization of a weak base and then set up the K_b expression. The conjugate acid of N_2H_4 has one additional H^+, so its formula is $N_2H_5^+$. We begin with the chemical equation and the K_b expression.

$$\text{N}_2\text{H}_4 + \text{H}_2\text{O} \rightleftharpoons \text{N}_2\text{H}_5^+ + \text{OH}^-$$

$$K_b = \frac{[\text{N}_2\text{H}_5^+][\text{OH}^-]}{[\text{N}_2\text{H}_4]}$$

Next we construct the concentration table.

	$N_2H_4 + H_2O \rightleftharpoons$	$N_2H_5^+$	$+OH^-$
Initial concentration (M)	0.25	0	0
Change in concentration caused by the ionization	$-x$	$+x$	$+x$
Concentration at equilibrium	$(0.25 - x)$ ≈ 0.25	x	x

Because x is so small, $[N_2H_4] \approx 0.25$ M. Substituting into the K_b expression, we get

$$\frac{(x)(x)}{0.25 - x} \approx \frac{(x)(x)}{0.25} = 9.6 \times 10^{-7}$$

Solving for x gives $x = 4.9 \times 10^{-4}$ M. This value represents the hydroxide ion concentration, from which we can calculate the pOH.

$$\text{pOH} = -\log(4.9\times10^{-4}) = 3.31$$

The pH of the solution can then be obtained from the relationship

$$\text{pH} + \text{pOH} = 14.00$$

Thus, $\text{pH} = 14.00 - 3.31 = 10.69$

To calculate the percentage ionization, we know the number of moles per liter of the base that has ionized. From the concentration table, we see that this value is also equal to x, the amount of N_2H_4 that ionizes per liter (i.e., the change in the N_2H_4 concentration). Therefore,

$$\text{Percentage ionization} = \frac{4.9\times10^{-4}}{0.25}\times100\% = 0.20\%$$

The base is 0.20% ionized.

Solved Example 10-17

Salicylic acid reacts with acetic acid to form aspirin, acetylsalicylic acid. A 0.200 M solution of salicylic acid has a pH of 1.836. Calculate the K_a and pK_a of salicylic acid.

Solution

The reaction involved is $\text{HSal} \rightleftharpoons \text{H}^+ + \text{Sal}^-$, with the ionization constant as

$$K_a = \frac{[\text{H}^+][\text{Sal}^-]}{[\text{HSal}]} \qquad (1)$$

$[\text{H}^+] = 10^{-\text{pH}} = 10^{-1.836} = 0.0146$ M. With the given values, the reaction can be expressed as

	HSal	$\rightleftharpoons \text{H}^+$	$+ \text{Sal}^-$
Initial concentration (M)	0.200	0	0
Change in concentration caused by the ionization	$-x$	$+x$	$+x$
Concentration at equilibrium	$(0.200-x)$	x	x

We know the $[\text{H}^+]$ is 0.0146 M, so $x = 0.0146$. Thus, $[\text{HSal}] = 0.200 - 0.0146 = 0.185$ M and $[\text{Sal}^-] = 0.0146$ M.

$$K_a = \frac{[\text{H}^+][\text{Sal}^-]}{[\text{HSal}]} = \frac{(0.0146)(0.0146)}{(0.185)} = 1.15\times10^{-3}$$

Therefore, $\text{p}K_a = -\log(K_a) = -\log(1.15\times10^{-3}) = 2.938$.

Solved Example 10-18

Phenol is an acidic organic compound for which $K_a = 1.3\times10^{-10}$. What is the pH of a 0.15 M solution of phenol in water?

Solution

We use the notation phenol and phenolate for the acid and its conjugate base, respectively. The reaction is

	Phenol	$\rightleftharpoons \text{H}^+$	$+ \text{Phenolate}^-$
Initial concentration (M)	0.15	0	0
Change in concentration caused by the ionization	$-x$	$+x$	$+x$
Concentration at equilibrium	$(0.15-x)$	x	x

The mass expression is $K_a = \dfrac{[\text{H}^+][\text{Phenolate}]}{[\text{Phenol}]} = 1.3\times10^{-10}$

If we assume that $x \ll 0.15$, a good assumption based upon the size of K_a, we can substitute the equilibrium values in to the mass action expression to get:

$$K_a = \frac{(x)(x)}{0.15} = 1.3\times10^{-10}$$

Solving gives $x = 4.4\times10^{-6}$ M $= [\text{H}^+]$. Therefore, $\text{pH} = -\log[\text{H}^+] = -\log(4.4\times10^{-6}) = 5.36$.

Solved Example 10-19

Calculate the concentrations of all the species produced in the ionization of 0.040 M H_2CO_3 as well as the pH of the solution.

Solution

The reaction is

	H_2CO_3	$\rightleftharpoons \text{H}^+$	$+ \text{HCO}_3^-$
Initial concentration (M)	0.040	0	0
Change in concentration	$-x$	$+x$	$+x$
Equilibrium concentration	$(0.040-x)$ ≈ 0.040	x	x

We know that some amount of H_2CO_3 ionizes; let us call this amount x. If x moles per liter of H_2CO_3 ionizes, then x moles per liter of H^+ and HCO_3^- are formed, and the concentration of H_2CO_3 is reduced by x. Substituting into the expression for K_{a1} gives

$$\mathrm{pH} = -\log(1.3\times10^{-4}) = 3.89$$

$$\frac{x^2}{(0.040-x)} \approx \frac{x^2}{0.040} = 4.5\times10^{-7}$$

Solving for x gives $x = 1.3 \times 10^{-4}$ M, so $[H^+] = [HCO_3^-] = 1.3\times10^{-4}$ M. From this, we can now calculate the pH.

$$\mathrm{pH} = -\log(1.3\times10^{-4}) = 3.89$$

Now let us calculate the concentration of CO_3^{2-}. We obtain this from the expression for K_{a2}.

$$K_{a_2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = 4.7\times10^{-11}$$

In our analysis, we concluded that we can use the approximations

$$[H^+]_{eq} \approx [H^+]_{\text{first step}}$$
$$[HCO_3^-]_{eq} \approx [HCO_3^-]_{\text{first step}}$$

Substituting the values obtained above gives us

$$\frac{(1.3\times10^{-4})[CO_3^{2-}]}{1.3\times10^{-4}} = 4.7\times10^{-11}\,\mathrm{M}$$

or $$[CO_3^{2-}] = 4.7\times10^{-11}\,\mathrm{M} = K_{a_2}$$

Solved Example 10-20

Ascorbic acid (vitamin C) is a diprotic acid, $H_2C_6H_6O_6$. Calculate $[H^+]$, pH and $[C_6H_6O_6^{2-}]$ in a 0.10 M solution of ascorbic acid.

Solution

$[H^+]$ is determined by the first protic equilibrium:

$$\begin{array}{ccccc} H_2C_6H_6O_6 & \rightleftharpoons & H^+ & + & HC_6H_6O_6^- \\ 1 & & 0 & & 0 \\ 1-x & & x & & x \end{array}$$

The mass action expression is: $K_{a_1} = 6.8\times10^{-5} = \dfrac{x^2}{0.10}$

So, $x = [H^+] = 2.6\times10^{-3}$ M and $\mathrm{pH} = -\log(2.6\times10^{-3}) = 2.58$.

The concentration of the anion, $[HC_6H_6O_6^-]$, is given almost entirely by the second ionization equilibrium:

$$HC_6H_6O_6^- \rightleftharpoons H^+ + C_6H_6O_6^{2-}$$

for which the mass action expression is:

$$K_{a_2} = \frac{[H^+][C_6H_6O_6^{2-}]}{[HC_6H_6O_6^-]} = 2.7\times10^{-12}$$

Using the value of x from the first step above gives:

$$2.7\times10^{-12} = \frac{(2.6\times10^{-3})[C_6H_6O_6^{2-}]}{(2.6\times10^{-3})}$$

So, $$[C_6H_6O_6^{2-}] = 2.7\times10^{-12}\ \mathrm{M}.$$

10.5 | RELATIVE STRENGTH OF ACIDS AND BASES

The strengths of acid and base can be understood in terms of Brönsted–Lowry concept. In aqueous solutions, the weak acids are Brönsted acids and, therefore, proton donors. Some examples are CH_3COOH, HSO_4^- and NH_4^+. In water, these participate in the following equilibria.

$$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-}$$

$$NH_4^+ + H_2O \rightleftharpoons H_3O^+ + NH_3$$

Notice that, in each case, the acid reacts with water to give H_3O^+ and the corresponding conjugate base. We can represent these reactions in a general way using HA to stand for the formula of the acid.

$$HA + H_2O \rightleftharpoons H_3O^+ + A^- \tag{10.10}$$

As you can see from the equations above, HA does not have to be electrically neutral; it can be a molecule such as CH_3COOH, a negative ion such as HSO_4^-, or a positive ion such as NH_4^+. The weak bases are weak Brönsted bases and are therefore proton acceptors. Examples are ammonia, NH_3, and acetate ion, CH_3COO^-. Their reactions with water are

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$
$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

In each instance, the base reacts with water to give OH^- and the corresponding conjugate acid. We can also represent these reactions by a general equation. If we represent the base by the symbol B, the reaction is

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

We have seen that the dissociation equilibrium between Brönsted–Lowry acids or bases is dynamic in nature. So we need to determine in which direction the reaction would proceed after a passage of time. This can be obtained by comparing the strength of two acids or bases involved in the equilibrium. For example, let us consider the dynamic equilibrium for dissociation of hydrochloric acid in aqueous medium.

$$\underset{\text{Strong acid}}{HCl(aq)} + H_2O(l) \rightleftharpoons H_3O^+(aq) + \underset{\text{Weak base}}{Cl^-(aq)}$$

The direction of reaction will be determined by relative strength of the two acids HCl and H_3O^+. Since HCl is a stronger acid than H_3O^+, it will donate protons and the solution will contain mainly Cl^- and H_3O^+ ions. So, the equilibrium would move in the direction of forward reaction, that is, it will move towards weaker acid and weaker base because stronger acid donates proton to stronger base.

Strong acids dissociate completely in aqueous medium and have weak conjugate bases. Other examples of strong acids and their weak conjugate bases are: H_2SO_4 (with HSO_4^- as weak conjugate base), HBr (with Br^-), HI (with I^-), HNO_3 (with NO_3^-), $HClO_4$ (with ClO_4^-) and so on.

Similarly, the dissociation of a weak acid can be considered using example of acetic acid.

$$\underset{\text{Weak acid}}{CH_3COOH(aq)} + H_2O(l) \rightleftharpoons \underset{\text{Strong base}}{CH_3COO^-(aq)} + H_3O^+(aq)$$

The extent of dissociation of acetic acid in aqueous medium is small and the forward reaction is not favored. The solution will mainly contain undissociated acetic acid. In other words, the conjugate base or the acetate ion shows a strong tendency to accept a proton. So the conjugate base of a weak acid is a strong base. Other examples of weak acids and their strong conjugate bases are nitrous acid and hydrofluoric acid.

Note: A strong acid has a weak conjugate base.
A weak acid has a strong conjugate base.
A strong base has a weak conjugate acid.
A weak base has a strong conjugate acid.

There is an inverse relationship between the strengths of the acid and base members of a conjugate pair. This is illustrated graphically in Fig. 10.2. From Eq. (10.8), the product of K_a and K_b is a constant, so the larger the value of K_a is, the smaller is the value of K_b. In other words, *the stronger the conjugate acid, the weaker is its conjugate base.*

An important consequence of this relationship is that it is not necessary to tabulate both K_a and K_b for the members of an acid–base pair; if one K is known, the other can be calculated. For example, the K_a for HCOOH and the K_b for NH_3 will be found in most tables of acid–base equilibrium constants. But these tables usually will not contain the equilibrium constants for the ions that are the conjugates. Thus, tables usually will not contain the K_b for $HCOO^-$ or the K_a for NH_4^+.

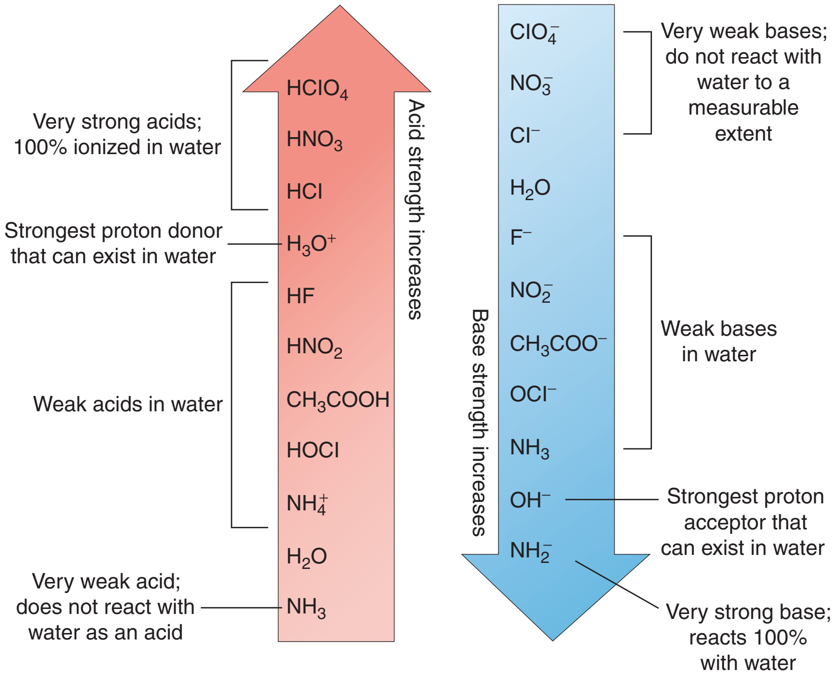


Figure 10.2 The relative strengths of conjugate acid–base pairs.

10.6 | IONIZATION OF POLYPROTIC ACIDS

Polybasic or polyprotic acids are those acids supplying more than one H^+ per molecule. For example, sulphuric acid, carbonic acid and phosphoric acid. These acids undergo ionization in a series of steps, each of which releases one proton. For weak polyprotic acids, such as H_2CO_3 and H_3PO_4, each step is in equilibrium. Even sulphuric acid, which we consider a strong acid, is not completely ionized. Loss of the first proton to yield the HSO_4^- ion is complete, but the loss of the second proton is incomplete and involves an equilibrium.

In water, the weak diprotic acid H_2CO_3 ionizes in two steps, each of which is an equilibrium that transfers an H^+ ion to a water molecule.

$$\begin{aligned} H_2CO_3 &\rightleftharpoons H^+ + HCO_3^- \\ HCO_3^- &\rightleftharpoons H^+ + CO_3^{2-} \end{aligned}$$

Each step has its own ionization constant, K_a, which we identify as K_{a1} for the first step and K_{a2} for the second. For carbonic acid,

$$K_{a1} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = 4.5 \times 10^{-7} \quad \text{and} \quad K_{a2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = 4.5 \times 10^{-11}$$

Mathematically, this can be explained as follows:

$$\begin{array}{lllll} & H_2CO_3 & \rightleftharpoons HCO_3^- & + & H^+ \\ \text{At } t = 0 & C_1 & \quad 0 & & 0 \\ \text{At } t = t_{eq} & C_1 - x & \quad x - y & & x + y \end{array}$$

Equilibrium constant = K_{a1}
Similarly

$$\begin{array}{llll} HCO_3^- & \rightleftharpoons CO_3^{2-} & + & H^+ \\ x - y & \quad y & & x + y \end{array}$$

Equilibrium constant = K_{a2}
Since $K_{a1} \gg K_{a2}$, therefore, $x \gg y$. Thus, $x - y \approx x$ and $x + y \approx x$. Then

$$K_{a1} = \frac{(x)(x)}{(C_1 - x)} \qquad K_{a2} \cong \frac{(y)(x)}{(x)} \cong y$$

Therefore,

$$[\mathrm{H}^+] = x + y \cong x$$
$$[\mathrm{HCO_3}^-] = x - y \cong x$$
$$[\mathrm{CO_3}^{2-}] = y$$

Each ionization makes a contribution to the total molar concentration of H^+, and one of our goals here is to relate the K_a values and the concentration of the acid to $[H^+]$. The principal factor that simplifies calculations involving many polyprotic acids is the large differences between successive ionization constants. For H_2CO_3, K_{a1} is much larger than K_{a2} (they differ by a factor of nearly 10,000). Similar differences between K_{a1} and K_{a2} are observed for many diprotic acids. One reason is that an H^+ is lost much more easily from the neutral H_2A molecule than from the HA^- ion. The stronger attraction of the opposite charges inhibits the second ionization. Typically, K_{a1} is greater than K_{a2} by a factor between 10^4 and 10^5, as the data in Table 10.4 show. For a triprotic acid, such as phosphoric acid, H_3PO_4, the second acid ionization constant is similarly greater than the third.

Table 10.4 Acid ionization constants for polyprotic acids

		Acid ionization constant for successive ionizations (25°C)		
Name	Formula	K_{a1}	K_{a2}	K_{a3}
Carbonic acid	H_2CO_3	4.5×10^{-7}	4.7×10^{-11}	
Hydrosulphuric acid	$H_2S(aq)$	9.5×10^{-8}	1×10^{-19}	
Phosphoric acid	H_3PO_4	7.1×10^{-3}	6.3×10^{-8}	4.5×10^{-13}
Arsenic acid	H_3AsO_4	5.6×10^{-3}	1.7×10^{-7}	4.0×10^{-12}
Sulphuric acid	H_2SO_4	Large	1.0×10^{-2}	
Selenic acid	H_2SeO_4	Large	1.2×10^{-2}	
Telluric acid	H_6TeO_6	2×10^{-8}	1×10^{-11}	
Sulphurous acid	H_2SO_3	1.2×10^{-2}	6.6×10^{-8}	
Selenous acid	H_2SeO_3	4.5×10^{-3}	1.1×10^{-8}	
Tellurous acid	H_2TeO_3	3.3×10^{-3}	2.0×10^{-8}	
Ascorbic acid (vitamin C)	$H_2C_6H_6O_6$	6.8×10^{-5}	2.7×10^{-12}	
Oxalic acid	$H_2C_2O_4$	5.6×10^{-2}	5.4×10^{-5}	
Citric acid (18°C)	$H_3C_6H_5O_7$	7.1×10^{-4}	1.7×10^{-5}	6.3×10^{-6}

Because K_{a1} is so much larger than K_{a2}, virtually all the H^+ in a solution of the acid comes from the first step in the ionization. In other words,

$$[\mathrm{H}^+]_{\text{total}} = [\mathrm{H}^+]_{\text{first step}} + [\mathrm{H}^+]_{\text{second step}}$$

where $[H^+]_{\text{first step}} \gg [H^+]_{\text{second step}}$. Therefore, we make the approximation that

$$[\mathrm{H}^+]_{\text{total}} \approx [\mathrm{H}^+]_{\text{first step}}$$

This means that as far as calculating the $[H^+]$ concentration is concerned, we can treat the acid as though it were a monoprotic acid and ignore the second step in the ionization. In addition, we have

$$[HCO_3^-]_{total} = [HCO_3^-]_{first\ step} - [CO_3^{2-}]_{second\ step}$$

However, since $[CO_3^{2-}]_{second\ step}$ is equal to $[H^+]_{second\ step}$, which is very small we can say that

$$[HCO_3^-]_{total} \approx [HCO_3^-]_{first\ step}$$

It is, therefore, reasonable to conclude that $[H^+]_{first\ step} = [HCO_3^-]_{first\ step}$

Note: In a solution that contains a polyprotic acid **as the only solute**, the concentration of the ion formed in the second step of the ionization equals K_{a2}.

Solved Example 10-21

A student planned an experiment that would use 0.10 M propionic acid, CH_3CH_2COOH. Calculate the value of $[H^+]$ and the pH for this solution. For propionic acid, $K_a = 1.34 \times 10^{-5}$.

Solution

First, we note that the only solute in the solution is a weak acid, so we know we will have to use K_a and write the equation for the ionization of the acid.

$$CH_3CH_2COOH \rightleftharpoons H^+ + CH_3CH_2COO^-$$

$$K_a = \frac{[H^+][CH_3CH_2COO^-]}{[CH_3CH_2COOH]}$$

The initial concentration of the acid is 0.10 M, and the initial concentrations of the ions are both 0 M. Then we construct the concentration table. All concentrations in the table are in moles per liter.

	$HC_3H_5O_2$	$\rightleftharpoons$	H^+	+	$C_3H_5O_2^-$
Initial concentrations (*M*)	0.10 (*C*)		0		0
Changes in concentrations caused by the ionization (*M*)	$C(1-\alpha)$ $-x$		$C\alpha + x$		$C\alpha + x$
Final concentrations at equilibrium (*M*)	$(0.10 - x)$ ≈ 0.10		x		x

Therefore, $x = C\alpha$ in this case and $C = 0.1$.

Notice that the equilibrium concentrations of H^+ and $CH_3CH_2COO^-$ are the same; they are represented by x. Anticipating that x will be very small, we make the simplifying approximation $(0.10 - x) \approx 0.10$, so we take the equilibrium concentration of CH_3CH_2COOH to be 0.10 *M*. Substituting these quantities into the K_a expression gives

$$K_a = \frac{[H^+][CH_3CH_2COO^-]}{[CH_3CH_2COOH]} = \frac{(x)(x)}{(0.10-x)} \approx \frac{(x)(x)}{(0.10)}$$
$$\approx 1.34 \times 10^{-5}$$

Solving for x yields $x = 1.2 \times 10^{-3}$. $x = [H^+]$. Finally, we calculate the pH

$$pH = -\log(1.2 \times 10^{-3}) = 2.92$$

First, we check to be sure our assumption was reasonable, and it is (0.10 – 0.0012 = 0.10 when rounded correctly). Also we see that the calculated pH is less than 7. This tells us that the solution is acidic, which it should be for a solution of an acid. Also, the pH is higher than it would be if the acid were strong. (A 0.10 *M* solution of a strong acid would have $[H^+] = 0.10$ and $pH = 1.0$). If we wish to further check the accuracy of the calculation, we can substitute the calculated equilibrium concentrations into the mass action expression. If the calculated quantities are correct, the reaction quotient should equal K_a. Let us do the calculation.

$$\frac{[H^+][CH_3CH_2COO^-]}{[CH_3CH_2COOH]} = \frac{(x)(x)}{(0.10)} = \frac{(1.2 \times 10^{-3})^2}{0.10}$$
$$= 1.4 \times 10^{-5} \approx K_a$$

The check works, so we know we have done the calculation correctly.

10.7 | FACTORS AFFECTING ACID STRENGTH

1. **Strength of binary acids:** Many of the binary compounds between hydrogen and non-metals, which we may represent by HX, H_2X, H_3X, etc., are acidic and are called **binary acids**. For example, weak acids (H_2O), H_2S, H_2Se, H_2Te of Group 16 and HF of Group 17; strong acids such as *HCl, *HBr and *HI of Group 17.

The relative strengths of acids correlate with the periodic table in two ways:

(a) The strengths of the acids increase from left to right within the same period: First, as we go left to right within a period, the increase in electronegativities causes the corresponding H—X bonds to become more polar, making the partial positive charge (δ+) on H greater. This makes it easier for the hydrogen to separate as H^+, so the molecule becomes a better proton donor. For example, as we go from S to Cl in the third period, the electronegativity increases and we find that HCl is a stronger acid than H_2S. A similar increase in electronegativity occurs on going from left to right in the second period, from O to F and HF is a stronger acid than H_2O.

(b) The strengths of acids increase from top to bottom within the same group: Second, acids become stronger from the top of a group to the bottom. Among the acids of the halogens, for example, the following is the order of relative acidity.

$$\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$$

Thus, HF is the weakest acid in the series, and HI is the strongest. The identical trend occurs in the series of the acids of Group 16 elements, having formulas of the general type H_2X. These trends in acidity are opposite to what we would expect on the basis of trends in electronegativities, which tell us that the H—F bond is more polar than the H—I bond and that the O—H bond is more polar than the H—S bond.

2. **Strength of H—X bond:** In understanding the proton donating ability of an acid, one of the most important factors to consider is the strength of the H—X bond. Breaking this bond is essential for hydrogen to separate as an H^+ ion, so anything that contributes to variations in bond strength will also impact variations in acid strength.

   In general, small atoms tend to form stronger bonds than large atoms. Moving horizontally within a period, atomic size varies relatively little, so the strengths of the H—X bonds are nearly the same. As a result, the most significant influence on acid strength is variations in the polarity of the H—X bonds. Descending a group, however, there is a significant increase in atomic size from one element to the next, which is accompanied by a rapid decrease in the H—X bond strength. Apparently, this more than compensates for the decrease in the polarity of the H—X bonds, and the molecules become better able to release protons as we go down a group. The net effect of the two opposing factors, therefore, is an increase in the strengths of the binary acids as we go from top to bottom in a group.

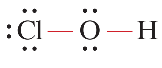
3. **Strengths of oxoacids:** Acids composed of hydrogen, oxygen, and some other element are called **oxoacids**. For example, H_2CO_3 carbonic acid in Group 14; HNO_3 nitric acid, HNO_2 nitrous acid, H_3PO_4 phosphoric acid, H_3PO_3 phosphorous acid, H_3AsO_4 arsenic acid, H_3AsO_3 arsenous acid in Group 15; H_2SO_4 sulphuric acid, H_2SO_3 sulphurous acid, H_2SeO_4 selenic acid, H_2SeO_3 selenous acid in Group 16; HFO hypofluorous acid, $HClO_4$ perchloric acid, $HClO_3$ chloric acid, $HClO_2$ chlorous acid, HClO hypochlorous acid, $HBrO_4$ perbromic acid, $HBrO_3$ bromic acid, HIO_4 periodic acid, HIO_3 iodic acid in Group 17.

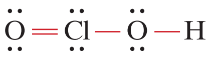
   When an oxoacid ionizes, the hydrogen that is lost as an H^+ comes from the same kind of bond in every instance, specifically, an O—H bond. The acidic strength of such acids is determined by how the groups attached to the oxygen affect the polarity of the O—H bond. If a group of atoms makes the O—H bond more polar, it will cause easier donation of H as H^+, and thereby increase the acidity of the molecule.

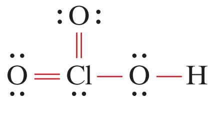
   It turns out that there are two principal factors that determine how the polarity of the O—H bond is affected.

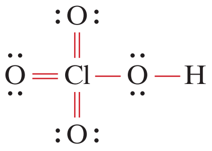
(a) Electronegativity of the central atom in the oxoacid: When the central atoms of oxoacids hold the same number of oxygen atoms, the acid strength increases from bottom to top within a group and from left to right within a period. For example, in Group 16, $HIO_4 < HBrO_4 < HClO_4$.

(b) Number of oxygen atoms attached to the central atom: In an oxoacid, lone oxygens pull electron density away from the central atom, which increases the central atom's ability to draw electron density away from the O—H bond. Therefore, the more lone oxygens that are attached to a central atom, the more polar will be the O—H bonds of the acid and the stronger will be the acid. For example, the oxoacids of chlorine, $HClO < HClO_2 < HClO_3 < HClO_4$. Comparing their structures, we have

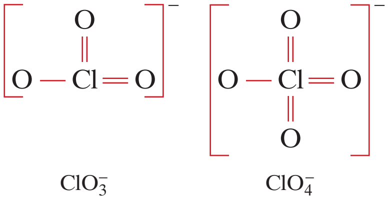

HClO


$HClO_2$


$HClO_3$


$HClO_4$

(c) **Delocalization of negative charge to the lone oxygen atoms:** For oxoacids, the lone oxygens play a part in determining the basicity of the anion formed in the ionization reaction. Consider the acids $HClO_3$ and $HClO_4$. $HClO_4$ is expected to be a stronger acid than $HClO_3$. Ionizations of their protons yield the anions ClO_3^- and ClO_4^-.



In an **oxoanion** (an anion formed from an oxoacid) the negative charge is delocalized over the oxygens. In the ClO_3^- ion, the single negative charge is spread over three oxygens, so each carries a charge of about –1/3. This is not a formal charge, but just implies that the charge of 1– is delocalized over three oxygens to give each a charge of –1/3. Similarly, in the ClO_4^- ion each oxygen carries a charge of about –1/4. The smaller negative charge on the oxygen atoms in ClO_4^- makes it less capable to attract H^+ ions from H_3O^+ than ClO_3^-, so ClO_4^- is a weaker base than ClO_3^-. Thus, the anion of stronger acid is the weaker base.

4. **Strength of other organic acids:** Acetic acid and most organic acids are characterized by the –COOH functional group. The delocalization of the electron on $–COO^-$ stabilizes the anion after the H^+ ionizes. If other electronegative groups such as halogens are bonded to carbon atoms near the –COOH group, they increase the strength of the acid. As a result, chloroacetic acid is a stronger acid than acetic acid. Dichloroacetic acid and trichloroacetic acids are increasingly stronger acids, $CH_3COOH < CH_2ClCOOH < CHCl_2COOH < CCl_3COOH$. Addition of each chlorine effectively withdraws more electron density from the —O—H bond, resulting in a weaker bond and a stronger acid.

Note: If conjugate base of an acid is stable, then the acid is a strong acid. If conjugate acid of a base is stable, then the base is a strong base.

10.8 | ACID–BASE NEUTRALIZATION – FORMATION OF SALTS

One of the most important properties of acids and bases is their reaction with each other, a reaction referred to as **neutralization**. For example, when solutions of hydrochloric acid, HCl(aq), and the base sodium hydroxide, NaOH(aq), are mixed the following reaction occurs.

$$HCl(aq)+NaOH(aq) \rightarrow NaCl(aq)+H_2O$$

When the reactants are combined in a 1-to-1 ratio by moles, the acidic and basic properties of the solutes disappear and the resulting solution is neither acidic nor basic. We say an *acid–base neutralization* has occurred

When acids and bases are mixed in the right proportions, salts are formed. It is important to understand how the salts are constituted in their normal state and how they behave in their solutions. Let us consider the example of sodium chloride. In solid state, the positively charged sodium ions and negatively charged chloride ions are held together by strong electrostatic forces. These electrostatic forces of attraction are inversely proportional to the dielectric of the medium in which the salt is dissolved, in this case water whose dielectric constant is 80. The sodium and chloride get separated and move freely in the solution.

Some terms associated with salts are as follows:

1. **Solvation:** The general term for the surrounding of a solute particle by solvent molecules is solvation. Ionic compounds are able to dissolve in water when the attractions between water dipoles and ions overcome the attractions of the ions for each other within the crystal.
2. **Hydration:** As the constituent ions become free, they become completely surrounded by water molecules. This phenomenon is called the hydration of ions. Hydration is just a special case of solvation.
3. **Ionization:** It refers to the formation of ions from a neutral molecule when dissolved in a solution. Ions are ionized on fusion or dissolution. This extent of ionization of any salt will thus depend on the strength of the bond and the extent of solvation of ions formed.

4. **Dissociation:** It refers to the separation of ions of substances that exist in ionic form in their solid state, when dissolved in solution. The terms dissociation and ionization are often used interchangeably but refer to different phenomena. A dissociation reaction is usually reversible.
5. **Decomposition:** The process of cleaving chemical compounds when subjected to chemical action, heat, electric current or biological agents is called decomposition. It can be a natural process or can be done artificially.

The various types of salts are as follows:

1. **Simple salts:** These salts are formed from simple acid–base neutralization reaction. These are further classified into:
   - **(a) Normal salts:** These are formed with the loss of all replaceable H^+ or OH^- ions. For example, NaCl, Na_2HPO_3, $NaNO_3$, K_2SO_4, etc.
   - **(b) Acidic salts:** These are formed due to incomplete neutralization of polybasic acids, and contain at least one replaceable hydrogen. These salts can be converted to normal salts by treating them with base. For example, $NaHSO_4$, $NaHCO_3$, NaH_2PO_4, Na_2HPO_4, etc.
   - **(c) Basic salts:** These salts are formed due to incomplete neutralization of polyacidic bases, and contain at least one hydroxyl group. These can be converted into normal salts by treating them with an acid. For example, Mg(OH)Cl, $Fe(OH)_2Cl$, $Bi(OH)_2Cl$, etc.
2. **Double salts:** These salts are addition compounds formed when two simple salts combine in stoichiometric amounts. These salts are stable in solid state only, and lose their identity in solution. When crystals of carnallite are dissolved in water, the solution shows the properties of K^+, Mg^{2+} and Cl^- ions. In the similar way, a solution of potassium alum shows the properties of K^+, Al^{3+} and SO_4^{2-} ions. These are both examples of double salts, which exist only in the crystalline state. Another example is Mohr salt $[(NH_4)Fe(SO_4)_2 \cdot 6H_2O]$.

$$\mathrm{KCl + MgCl_2 + 6H_2O \rightarrow \underset{(Carnallite)}{KCl \cdot MgCl_2 \cdot 6H_2O}}$$

$$\mathrm{K_2SO_4 + Al_2(SO_4)_3 + 24H_2O \rightarrow \underset{(Potassium\ alum)}{K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O}}$$

3. **Complex salts:** These salts are formed due to combination of simple salts or molecular compounds, and they retain their identity in solid as well as solution state. When the compounds $CuSO_4 \cdot 4NH_3 \cdot H_2O$ and $Fe(CN)_2 \cdot 4KCN$ are dissolved in water, they do not form simple ions—Cu^{2+}, or Fe^{2+} and CN^- but instead their complex ions remain intact. Thus, the cuproammonium ion $[Cu(H_2O)_2(NH_3)_4]^{2+}$ and the ferrocyanide ion $[Fe(CN)_6]^{4-}$ exist as distinct entities both in solid and in solution. These are complex salts and are represented by the use of square brackets. Compounds containing these ions are called **coordination compounds**.

$$\mathrm{CuSO_4 + 4NH_3 + H_2O \rightarrow \underset{(Tetrammine\ copper(II)\ sulphate\ monohydrate)}{CuSO_4 \cdot 4NH_3 \cdot H_2O}}$$

$$\mathrm{Fe(CN)_2 + 4KCN \rightarrow \underset{Potassium\ ferrocyanide}{Fe(CN)_2 \cdot 4KCN}}$$

4. **Mixed salts:** These salts are called so because when dissolved in a solution, they dissociate to form more than one cation (apart from H^+) or more than one anion (apart from OH^-). For example, $CaOCl_2$, $KNaSO_4$, $NaNH_4 \cdot HPO_4$.

10.9 | pH CALCULATION OF SINGLE MONOBASIC ACID OR MONOACIDIC BASE

For calculating the pH of single monobasic acid or monoacidic base, consider the following cases:

Case 1: For a strong acid HA with concentration *C*. In aqueous solution:

$$\begin{array}{lccc} & \mathrm{HA} & \rightleftharpoons \mathrm{H^+} & + \mathrm{A^-} \\ \text{At } t = 0 & C & 0 & 0 \\ \text{At } t = t_{eq} & 0 & C & C \end{array}$$

Then, $\mathrm{pH} = -\log [H^+] = -\log C$

Case 2: For a strong base BOH with concentration C. In aqueous solution:

$$\begin{array}{lccc} & \text{BOH} & \rightleftharpoons \text{B}^+ & +\text{OH}^- \\ \text{At } t=0 & C & 0 & 0 \\ \text{At } t=t_{\text{eq}} & 0 & C & C \end{array}$$

Then, $\text{pOH} = -\log\,[\text{OH}^-] = -\log C$

We know that, $\text{pH} + \text{pOH} = \text{p}K_w = 14$ (at 25 °C). Therefore,

$$\text{pH} = 14 + \log C$$

Case 3: For a weak acid HA with concentration C, equilibrium constant K_a and dissociation constant ($\alpha \ll 1$). In aqueous solution:

$$\begin{array}{lccc} & \text{HA} & \rightleftharpoons \text{H}^+ & + \ \text{A}^- \\ \text{At } t=0 & C & 0 & 0 \\ \text{At } t=t_{\text{eq}} & C(1-\alpha) & C\alpha & C\alpha \end{array}$$

As $\alpha \ll 1$, $(1 - \alpha) \approx 1$, the equilibrium constant can be written as

$$K_a = \frac{(C\alpha)(C\alpha)}{C(1-\alpha)} = C\alpha^2$$

$$\alpha = \sqrt{\frac{K_a}{C}}$$

$$[\text{H}^+] = C\alpha = \sqrt{K_a C}$$

$$\text{pH} = -\frac{1}{2}[\log K_a + \log C]$$

Case 4: For a weak base BOH with concentration C, equilibrium constant K_b and dissociation constant ($\alpha \ll 1$). In aqueous solution:

$$\begin{array}{lccc} & \text{BOH} & \rightleftharpoons \text{B}^+ & + \ \text{OH}^- \\ \text{At } t=0 & C & 0 & 0 \\ \text{At } t=t_{\text{eq}} & C(1-\alpha) & C\alpha & C\alpha \end{array}$$

As $\alpha \ll 1$, $(1 - \alpha) \approx 1$, the equilibrium constant can be written as

$$K_b = \frac{(C\alpha)(C\alpha)}{C(1-\alpha)} = C\alpha^2$$

$$\alpha = \sqrt{\frac{K_b}{C}}$$

$$[\text{OH}^-] = C\alpha = \sqrt{K_b C}$$

$$\text{pOH} = -\frac{1}{2}[\log K_b + \log C]$$

We know that $\text{pH} = 14 - \text{pOH}$ (at 25°C). Therefore,

$$\text{pH} = 14 + \frac{1}{2}[\log K_b + \log C]$$

Case 5: Strong acid or strong base with extremely low concentrations ($C \ll 10^{-6}$ M). For example, for NaOH (10^{-8} M), if we just calculate pH as we do in normal case of a strong base

$$\begin{array}{lccc} & \text{NaOH} & \rightleftharpoons \text{Na}^+ & +\text{OH}^- \\ \text{At } t=0 & 10^{-8} & 0 & 0 \\ \text{At } t=t_{\text{eq}} & 0 & 10^{-8} & 10^{-8} \end{array}$$

$$[\text{OH}^-] = 10^{-8} \Rightarrow \text{pOH} = 8 \Rightarrow \text{pH} = 6$$

But the pH of any base has to be greater than 7 (at 25°C). So the method is not correct and contribution of H_2O towards $[OH^-]$ has to be taken into account. So,

$$\begin{array}{llll} & \mathrm{NaOH} & \rightleftharpoons \mathrm{Na^+} & + \mathrm{OH^-} \\ \text{At } t = 0 & 10^{-8} & 0 & 0 \\ \text{At } t = t_{\mathrm{eq}} & 0 & 10^{-8} & 10^{-8} + x \\ \text{Also,} & \mathrm{H_2O} \rightleftharpoons & \mathrm{H^+} & + \mathrm{OH^-} \\ & & x & (x + 10^{-8}) \end{array}$$

Then,

$$10^{-14} = [\mathrm{H^+}][\mathrm{OH^-}] = x(x + 10^{-8})$$

$$x^2 + 10^{-8}x - 10^{-14} = 0$$

$$x = \frac{-10^{-8} + \sqrt{10^{-16} \times 4 \times 10^{-14}}}{2} = \frac{19 \times 10^{-8}}{2} = 9.5 \times 10^{-8}$$

Therefore,

$$[\mathrm{H^+}] = 10^{-8} + 9.5 \times 10^{-8} = 10.5 \times 10^{-8}$$

$$\mathrm{pH} = 8 - \log 10.5 = 6.97$$

Note: In all such questions, a simple trick to get the answer for any base, if we have the analogous case for an acid, is to replace $[H^+]$ by $[OH^-]$, pH by pOH and K_a by K_b.

Charge and Mass Balance

Equilibria existing in the solution in case of monoprotic acid can be expressed as

$$\mathrm{HA} \rightleftharpoons \mathrm{H^+} + \mathrm{A^-} \qquad K_a = \frac{[\mathrm{H^+}][\mathrm{A^-}]}{[\mathrm{HA}]_{\text{undissociated}}} \tag{10.11}$$

$$\mathrm{H_2O} \rightleftharpoons \mathrm{H^+} + \mathrm{OH^-} \qquad K_w = [\mathrm{H^+}][\mathrm{OH^-}] \tag{10.12}$$

Assuming initial concentration of HA = C or $[HA]_0 = C$. Applying charge balance, total charge is constant, so

$$\underset{\text{(Initial charge)}}{0} = \underset{\text{(Charge of H}^+\text{ is}+1)}{1 \times \mathrm{H^+}} - \underset{\text{(Charge of A}^-\text{ is}-1)}{1 \times \mathrm{A^-}} - \underset{\text{(Charge of OH}^-\text{ is}-1)}{1 \times [\mathrm{OH^-}]}$$

Therefore, $[\mathrm{A^-}] = [\mathrm{H^+}] - [\mathrm{OH^-}]$

$$[\mathrm{A^-}] = [\mathrm{H^+}] - \frac{K_w}{[\mathrm{H^+}]} \qquad (10.13) \quad [(\text{Using } (10.12)]$$

Applying mass balance on A

$$\underset{\text{(Since only 1 atom of A is present in HA)}}{1 \times [\mathrm{HA}]_0} = \underset{\text{(Since }[\mathrm{HA}]_{\text{dissociated}}\text{ contains 1 atom of A)}}{1 \times [\mathrm{HA}]_0} + \underset{\text{(Since A}^-\text{ contains 1 atom of A)}}{1 \times [\mathrm{A^-}]}$$

Therefore,

$$C = [\mathrm{HA}]_{\text{undissociated}} + [\mathrm{A^-}]$$

$$[\mathrm{HA}]_{\text{undissociated}} = C - [\mathrm{A^-}]$$

$$[\mathrm{HA}]_{\text{undissociated}} = C - [\mathrm{H^+}] + \frac{K_w}{[\mathrm{H^+}]} \qquad (10.14) \quad [\text{Using } (10.13)]$$

Substituting $[A^-]$ and $[HA]_{\text{undissociated}}$ from Eqs. (10.13) and (10.14) in Eq. (10.11), we get

$$K_a = \frac{[H^+]\left([H^+] - \dfrac{K_w}{[H^+]}\right)}{\left(C - [H^+] + \dfrac{K_w}{[H^+]}\right)} \tag{10.15}$$

This equation consists of only one variable $[H^+]$ and thus pH can be calculated as –log $[H^+]$. Simplification of Eq. (10.15) for various cases:

Case 1: Strong acid ($C > 10^{-6}$ M)

For a strong acid, $\alpha \to 1$ or $K_a \to \infty$. Therefore,

$$C - [H^+] + \frac{K_w}{[H^+]} = 0$$

Now, $C > 10^{-6}$ M. Therefore, contribution of H^+ from H_2O can be neglected. $\dfrac{K_w}{[H^+]}$ is a term due to contribution by H_2O equilibrium. Therefore,

$$C - [H^+] = 0 \to [H^+] = C \text{ or pH} = -\log C$$

Case 2: Strong acid ($C \le 10^{-6}$ M)

For a strong acid, $\alpha \to 1$ or $K_a \to \infty$. In this case H^+ contribution from H_2O cannot be neglected. Therefore,

$$C - [H^+] + \frac{K_w}{[H^+]} = 0$$

$$[H^+]^2 - C[H^+] - K_w = 0$$

$$[H^+] = \frac{C + \sqrt{C^2 + 4K_w}}{2}$$

$$\text{pH} = -\log[H^+]$$

Case 3: Weak acid ($C > 10^{-6}$ M)

In this case contribution of H^+ from H_2O can be neglected or $\dfrac{K_w}{[H^+]}$ term can be neglected.

Therefore,

$$K_a = \frac{[H^+][H^+]}{(C - [H^+])}$$

$$[H^+]^2 + K_a[H^+] - K_a \times C = 0$$

or,

$$[H^+] = \frac{-K_a + \sqrt{K_a^2 + 4K_a \times C}}{2}$$

$$\text{pH} = -\log[H^+]$$

Case 4: Weak acid ($C \le 10^{-6}$ M)

In this case no approximation can be made to Eq. (10.15).

10.10 | pH CALCULATION OF A MIXTURE OF TWO ACIDS OR BASES

For calculation of pH for a mixture of two acids or two bases, consider the following cases.

Case 1: Mixture of two strong monobasic acids. Given:

HA_1	HA_2
Conc. C_1	Conc. C_2
Molar conc. M_1	Molar conc. M_2
Volume V_1	Volume V_2

Then, for HA_1

$$\begin{array}{lcccccccc}
 & HA_1 & \rightleftharpoons H^+ & +\ A_1^- & \qquad & HA_1 & \rightleftharpoons H^+ & +A_1^- \\
\text{At } t=0 & M_1V_1 & 0 & 0 & & C_2 & 0 & 0 \\
\text{At } t=t_{\text{eq}} & 0 & M_1V_1 & M_1V_1 & & 0 & C_1 & C_2 \\
 & & +M_2V_2 & & & & +C_2 &
\end{array}$$

Similarly for HA_2

$$\begin{array}{lcccccccc}
 & HA_2 & \rightleftharpoons H^+ & +\ A_2^- & \qquad & HA_2 & \rightleftharpoons H^+ & +A_2^- \\
\text{At } t=0 & M_2V_2 & 0 & 0 & & C_1 & 0 & 0 \\
\text{At } t=t_{\text{eq}} & 0 & M_2V_2 & M_2V_2 & & 0 & C_1 & C_1 \\
 & & +M_1V_1 & & & & +C_2 &
\end{array}$$

Therefore,

$$[H^+]_{\text{final}} = \frac{M_1V_1 + M_2V_2}{V_1 + V_2} \qquad\qquad [H^+] = C_1 + C_2$$

$$\text{pH} = -\log\frac{M_1V_1 + M_2V_2}{V_1 + V_2} \qquad\qquad \text{pH} = -\log(C_1 + C_2)$$

Case 2: Mixture of a strong monobasic acid and a weak monobasic acid. Given:

HA_1 (strong)	HA_2 (weak)
Conc. C_1	Conc. C_2
	Equilibrium constant K_{a2}
	Dissociation constant α_2

Then, for HA_1

$$\begin{array}{lcccc}
 & HA_1 & \rightleftharpoons & H^+ + & A_1^- \\
\text{At } t=0 & C_1 & & 0 & 0 \\
\text{At } t=t_{\text{eq}} & 0 & & C_1 & C_1 \\
 & & & +C_2\alpha_2 &
\end{array}$$

Similarly for HA_2

$$\begin{array}{lcccc}
 & HA_2 & \rightleftharpoons & H^+ + & A_2^- \\
\text{At } t=0 & C_2 & & 0 & 0 \\
\text{At } t=t_{\text{eq}} & C_2(1-\alpha_2) & & C_2\alpha_2 & C_2\alpha_2 \\
 & & & +C_1 &
\end{array}$$

$$K_a = \frac{(C_1 + C_2\alpha_2)(C_2\alpha_2)}{C_2(1-\alpha_2)} = (C_1 + C_2\alpha_2)(\alpha_2)$$

$$C_2\alpha_2^2 + C_1\alpha_2 - K_a = 0$$

$$\alpha_2 = \frac{-C_1 + \sqrt{C_1^2 + 4K_aC_2}}{2C_2}$$

We can get the exact value of α by solving the above quadratic equation. However, a simple assumption using the common ion effect, will make the problem very simple. Using common ion effect, we can say that $[H^+]$ contribution from the weak acid HA_2 can be neglected. Therefore,

$$[H^+] = C_1 + C_2\alpha_2 \cong C_1$$

$$\text{pH} \cong -\log C_1$$

Case 3: Mixture of two weak monobasic acids. Given:

HA_1	HA_2
Conc. C_1	Conc. C_2
Equilibrium constant K_{a1}	Equilibrium constant K_{a2}
Dissociation constant α_1 $(\alpha_1 \ll 1)$	Dissociation constant α_2 $(\alpha_2 \ll 1)$

Then, for HA_1

$$\begin{array}{lcccc} & HA_1 & \rightleftharpoons & H^+ + & A_1^- \\ \text{At } t=0 & C_1 & & 0 & 0 \\ \text{At } t=t_{eq} & C_1(1-\alpha_1) & & C_1\alpha_1 & C_1\alpha_1 \\ & & & +C_2\alpha_2 & \end{array}$$

Similarly for HA_2

$$\begin{array}{lcccc} & HA_2 & \rightleftharpoons & H^+ + & A_2^- \\ \text{At } t=0 & C_2 & & 0 & 0 \\ \text{At } t=t_{eq} & C_2(1-\alpha_2) & & C_2\alpha_2 & C_2\alpha_2 \\ & & & +C_1\alpha_1 & \end{array}$$

Therefore,

$$K_{a1} = \frac{(C_1\alpha_1 + C_2\alpha_2)(C_1\alpha_1)}{C_1} \qquad (\text{as } \alpha_1 \ll 1)$$

$$K_{a1}C_1 = (C_1\alpha_1 + C_2\alpha_2)(C_1\alpha_1) \tag{10.16}$$

Similarly,

$$K_{a2} = \frac{(C_1\alpha_1 + C_2\alpha_2)(C_2\alpha_2)}{C_2} \qquad (\text{as } \alpha_2 \ll 1)$$

$$K_{a2}C_2 = (C_1\alpha_1 + C_2\alpha_2)(C_2\alpha_2) \tag{10.17}$$

Adding Eqs. (10. 16) and (10. 17), we get

$$K_{a1}C_1 + K_{a2}C_2 = (C_1\alpha_1 + C_2\alpha_2)^2$$

$$(C_1\alpha_1 + C_2\alpha_2) = \sqrt{K_{a1}C_1 + K_{a2}C_2} = [H^+]$$

Therefore,

$$pH = -\frac{1}{2}\log[K_{a1}C_1 + K_{a2}C_2]$$

Note: Similarly we can get the following results in the case of mixture of monoacidic bases.

1. Mixture of two strong bases B_1OH and B_2OH with concentrations C_1 and C_2.

$$pOH = -\log(C_1 + C_2)$$

2. Mixture of a strong base B_1OH and a weak base B_2OH with concentrations C_1 and C_2 and equilibrium constants K_{b1} and K_{b2}, respectively.

$$pOH = -\log C_1$$

3. Mixture of two weak bases B_1OH and B_2OH with concentrations C_1 and C_2 and equilibrium constants K_{b1} and K_{b2}, respectively.

$$pOH = -\frac{1}{2}\log[K_{b1}C_1 + K_{b2}C_2]$$

Solved Example 10-22

Calculate the $[H^+]$ in a solution containing 0.1 M HCOOH and 0.1 M HOCN. [K_a for HCOOH and HOCN are 1.8×10^{-4} and 3.3×10^{-4}, respectively].

Solution

The reaction is

$$\begin{array}{ccc} \mathrm{HCOOH} & \rightleftharpoons & \mathrm{H^+} + \mathrm{HCOO^-} \\ 0.1-a & & a+b \qquad a \end{array}$$

and

$$\begin{array}{ccc} \mathrm{HOCN} & \rightleftharpoons & \mathrm{H^+} + \mathrm{OCN^-} \\ 0.1-b & & b+a \qquad b \end{array}$$

$$K_{a(\mathrm{HCOOH})} = \frac{(a+b)a}{0.1-a} \qquad (1)$$

$$K_{a(\mathrm{HOCN})} = \frac{(a+b)b}{0.1-b} \qquad (2)$$

Dividing Eq. (1) by Eq. (2), we get

$$\frac{a}{b} = \frac{1.8}{3.3} \Rightarrow b = 1.83a$$

Now solving, we get $a = 2.52 \times 10^{-3}$ M and $b = 4.61 \times 10^{-3}$ M. Therefore, $[H^+] = a + b = 7.13 \times 10^{-3}$ M.

pH of Mixture of Strong Acids in Water

In this case, it is advised to add the sum of milliequivalents of all the acids, which will furnish the same number of milliequivalents of hydrogen ions in the solution. Suppose we have two strong acids HA and HB, (i.e., $a = 1$) then

$$[H^+]_{\text{total milliequivalents}} = N_A V_A + N_B V_B = \Sigma\text{milliequivalents of acids.}$$

Now, molarity of $[H^+] = \dfrac{[H^+]_{\text{total milliequivalents}}}{\text{Total volume}}$ and hence $\text{pH} = -\log[H^+]_{\text{molarity}}$.

Solved Example 10-23

One liter of HCl (pH = 2) is mixed with two liters of an acid HNO_3 (pH = 3). Calculate the pH of the resultant acid mixture.

Solution

We know that $N_1V_1 + N_2V_2 = N_fV_f$. Substituting given values and $V_f = V_1 + V_2$ in this equation, we get

$$10^{-2} \times 1 + 10^{-3} \times 2 = N_f \times 3 \Rightarrow N_f = 4 \times 10^{-3}$$

Therefore, $\text{pH} = -\log(4 \times 10^{-3}) = 2.3980$

10.11 | pH CALCULATION FOR POLYPROTIC ACIDS

For calculation of pH of polyprotic acids, consider the following cases:

Case 1: Strong polyprotic acid H_2A with concentration C and equilibrium constant K_{a2}.

$$\begin{array}{lccccc} & \mathrm{H_2A} & \rightleftharpoons & \mathrm{H^+} & + & \mathrm{HA^-} \\ \text{At } t = 0 & C & & 0 & & 0 \\ \text{At } t = t_{eq} & 0 & & C + x & & C - x \end{array}$$

Similarly,

$$\begin{array}{lccccc} & \mathrm{HA^-} & \rightleftharpoons & \mathrm{H^+} & + & \mathrm{A^{2-}} \\ \text{At } t = t_{eq} & C - x & & x + C & & x \end{array}$$

Therefore,

$$K_{a2} = \frac{(x+C)(x)}{(C-x)}$$

Solving the above equation, we get the value of x

$$[H^+] = C + x$$
$$pH = -\log(C+x)$$

Case 2: Weak polyprotic acid H_3A with concentration C_1. Given that the equilibrium constants are K_{a1}, K_{a2} and K_{a3}, such that $K_{a1} \gg K_{a2} \gg K_{a3}$.

$$\begin{array}{lccccccl} & H_3A & \rightleftharpoons & H^+ & + & H_2A^- & & (\text{Equilibrium constant } K_{a1}) \\ \text{At } t = 0 & C_1 & & 0 & & 0 & & \\ \text{At } t = t_{eq} & C_1 - x & & x+y+z & & x-y & & \end{array}$$

Similarly,

$$\begin{array}{lccccccl} & H_2A^- & \rightleftharpoons & H^+ & + & HA^{2-} & & (\text{Equilibrium constant } K_{a2}) \\ \text{At } t = t_{eq} & x-y & & x+y+z & & y-z & & \end{array}$$

And

$$\begin{array}{lccccccl} & HA^{2-} & \rightleftharpoons & H^+ & + & A^{3-} & & (\text{Equilibrium constant } K_{a3}) \\ \text{At } t = t_{eq} & y-z & & x+y+z & & z & & \end{array}$$

Since $K_{a1} \gg K_{a2} \gg K_{a3}$, therefore $x \gg y \gg z$. Therefore,

$$x + y + z \approx x;\ x - y \approx x \text{ and } y - z \approx y$$

Therefore,

$$K_{a1} = \frac{x^2}{C-x}$$

Solving for x, we get

$$[H^+] = x + y + z \cong x$$
$$pH = -\log x$$

Note: To calculate pH for a weak polyprotic acid, consider the first dissociation step only to calculate the pH.

10.12 | HYDROLYSIS OF SALTS AND pH OF THEIR SOLUTIONS

Salt dissolves in water to produce both a cation and an anion. The cation has the potential to act as an acid and the anion as a base. They can exist as hydrated ions in aqueous solutions or interact with water to re-form acids and bases. The reaction of a cation as an acid or an anion as a base is known as a **hydrolysis** reaction. The interaction between water and cations and/or anions of the salt alters the pH of the solution.

Hydrolysis is reverse of neutralization

$$\text{Salt} + H_2O \rightleftharpoons \text{Acid} + \text{Base}$$

To decide if any given salt will affect the pH of an aqueous solution, we must examine each of its ions and see what it alone might do. There are four possibilities:

1. If neither the cation nor the anion can affect the pH, the solution should be neutral.
2. If only the cation of the salt is acidic, the solution will be acidic.

3. If only the anion of the salt is basic, the solution will be basic.
4. If a salt has a cation that is acidic and an anion that is basic, the pH of the solution is determined by the *relative* strengths of the acid and base based on the K_a and K_b of the ions.

Hydrolysis in strong acids, strong bases weak acids and weak bases

1. **Anions of strong acids and cations of strong bases do not undergo hydrolysis reactions:** Some ions do not undergo hydrolysis, so they do not have acid or base character in water and will not change the pH of pure water from 7.0. For example, in the ionization process of HCl, the forward reaction is 100% complete, so the reverse reaction does not occur in water. Thus we notice that the Cl^- ion, in spite of being a conjugate base, does not exhibit proton-accepting ability in water to form an HCl molecule. Hence, the Cl^- ion does not undergo hydrolysis. Similarly, the other anions of strong acids (i.e., NO_3^-, ClO_4^-, Br^- and I^-) do not undergo hydrolysis reactions. The same is true for the cations of strong bases (e.g., Na^+, K^+, Ca^{2+} and Mg^{2+} and other alkali metal and alkaline earth metal ions). All of them exist as independent, hydrated ions in aqueous solution and so do not undergo hydrolysis.
2. **Anions of weak acids (i.e., their conjugate bases) undergo hydrolysis in aqueous solution, producing weakly basic solutions:** Let us the ionization equilibrium for the weak acid HClO.

$$HClO(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + ClO^-(aq)$$

   Since this reaction reaches a point of equilibrium favoring the reactants on the left, the ClO^- demonstrates proton-accepting ability in water. When this anion is added to water as part of a salt, it exhibits its weakly basic nature by producing a small concentration of hydroxide ion. The following equation represents the hydrolysis reaction of the hypochlorite ion.

$$ClO^-(aq) + H_2O(l) \rightleftharpoons HClO(aq) + OH^-(aq)$$

   The extent of hydrolysis of anions is generally quite small, however, so the equilibrium lies far to the left.

   Anionic hydrolysis can be represented as

$$A^- + H_2O \rightleftharpoons HA + OH^-$$

3. **Cations (conjugate acids) of weak bases undergo hydrolysis in aqueous solution, producing weakly acidic solutions:** Let us now consider the ionization equilibrium of a weak base, ammonia. It reacts with water to produce small concentrations of NH_4^+ and OH^- ions. Since this is also an equilibrium situation, we can conclude that the NH_4^+ ion demonstrates proton-donating properties in the reverse reaction. When the ammonium ion is placed in water as part of a salt, it exhibits a weakly acidic nature by producing a small concentration of hydronium ion. The hydrolysis of the ammonium ion is illustrated by the following equation.

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NH_3(aq)$$

   Cationic hydrolysis can be represented as

$$B^+ + H_2O \rightleftharpoons BOH + H^+$$

   Based on these, we can now explore the behavior of salts of the following types, in their aqueous solutions.

Salt of Strong Acid and Strong Base

Salt of a strong acid and a strong base does not undergo salt hydrolysis. The pH in such cases is

$$pH = \frac{1}{2} pK_w$$

Hence if $pK_w = 14$, then pH = 7. For example, NaCl, KNO_3, etc.

Consider NaCl

$$Na^+ Cl^- + H_2O \rightleftharpoons Na^+ + OH^- + Cl^- + H^+$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

Therefore,

$$\text{pH} = \frac{\text{p}K_\text{w}}{2} = 14 \quad (\text{at } 25\,^\circ\text{C})$$

Salt of Weak Acid and Strong Base

Consider the example of CH_3COONa which is a salt of weak acid (CH_3COOH) and a strong base (NaOH). It undergoes complete dissociation in aqueous solution.

$$CH_3COONa\ (aq) \rightarrow CH_3COO^-(aq) + Na^+(aq)$$

We have seen above that acetate ions undergo hydrolysis in water to form acetic acid and hydroxide ions.

$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$$

Acetic acid being a weak acid will remain unionized in water and the concentration of hydroxide ions will make the solution alkaline, so the pH of the solution will be more than 7. The hydrolysis constant is K_h expressed as

$$K_\text{h} = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} \qquad (10.18)$$

We know that $K_\text{w} = [H^+][OH^-]$ and $K_\text{a} = \dfrac{[CH_3COO^-][H^+]}{CH_3COOH}$. Comparing with the above equation, we get

$$K_\text{h} = \frac{K_\text{w}}{K_\text{a}} \qquad (10.19)$$

From Eq. (10.18), we have

$$[OH^-] = \frac{K_\text{h} \times [CH_3COO^-]}{[CH_3COOH]} = \frac{K_\text{w}}{K_\text{a}}\frac{[CH_3COO^-]}{[CH_3COOH]}$$

Taking log on both sides, we get

$$\log[OH^-] = \log K_\text{w} - \log K_\text{a} + \log\frac{[\text{Salt}]}{[\text{Acid}]}$$

or

$$-\text{pOH} = -\text{p}K_\text{w} + \text{p}K_\text{a} + \log\frac{[\text{Salt}]}{[\text{Acid}]} \Rightarrow \text{p}K_\text{w} - \text{pOH} = \text{p}K_\text{a} + \log\frac{[\text{Salt}]}{[\text{Acid}]}$$

$$\text{pH} = \text{p}K_\text{a} + \log\frac{[\text{Salt}]}{[\text{Acid}]} \qquad (10.20)$$

In hydrolysis of salts, the degree of dissociation is replaced by **degree of hydrolysis**, which is represented by h. Substituting the concentrations in Eq. (10.18) in terms of C and h from the reaction

$$\underset{C(1-h)}{CH_3COO^-(aq)} + H_2O(l) \rightleftharpoons \underset{Ch}{CH_3COOH(aq)} + \underset{Ch}{OH^-(aq)}$$

we get
$$K_h = \frac{Ch \times Ch}{C(1-h)} = \frac{Ch^2}{1-h}$$

As $h \ll 1$, we have
$$Ch^2 = \frac{K_w}{K_a} \Rightarrow h = \sqrt{\frac{K_w}{K_a C}}$$

Now,
$$[\mathrm{OH^-}] = Ch = C \times \sqrt{\frac{K_w}{K_a C}} = \sqrt{\frac{K_w C}{K_a}}$$

Similarly,
$$[\mathrm{H^+}] = \frac{K_w}{[\mathrm{OH^-}]} = \sqrt{\frac{K_w K_a}{C}}$$

Taking log on both sides, we get

$$-\log[\mathrm{H^+}] = \frac{1}{2}\log K_w - \frac{1}{2}\log K_a + \frac{1}{2}\log C = \frac{1}{2}(\mathrm{p}K_w + \mathrm{p}K_a + \log C)$$

Therefore,
$$\mathrm{pH} = 7 + \frac{1}{2}\mathrm{p}K_a + \frac{1}{2}\log C \qquad (10.21)$$

Salt of Strong Acid and Weak Base

Consider the example of NH_4Cl which is a salt of a strong acid (HCl) and a weak base (NH_4OH). It undergoes complete dissociation in aqueous medium.

$$\mathrm{NH_4Cl(aq)} \rightarrow \mathrm{NH_4^+(aq)} + \mathrm{Cl^-(aq)}$$

We have seen that ammonium ions undergo hydrolysis to form ammonia and H^+ ions.

$$\mathrm{NH_4^+(aq)} + \mathrm{H_2O(l)} \rightleftharpoons \mathrm{NH_4OH(aq)} + \mathrm{H^+}$$

Ammonium hydroxide is a weak base, so it remains unionized in solution and the concentration of H^+ ions makes the solution acidic and pH of the solution is lower than 7. The hydrolysis constant is K_h expressed as

$$K_h = \frac{[\mathrm{NH_4OH}][\mathrm{H^+}]}{[\mathrm{NH_4^+}]} \qquad (10.22)$$

We know that $K_w = [\mathrm{H^+}][\mathrm{OH^-}]$ and $K_b = \dfrac{[\mathrm{NH_4^+}]\times[\mathrm{OH^-}]}{[\mathrm{NH_4OH}]}$. Comparing with the above equation, we get

$$K_h = \frac{K_w}{K_b} \qquad (10.23)$$

From Eq. (10.22), we have
$$[\mathrm{H^+}] = \frac{K_h \times [\mathrm{NH_4^+}]}{[\mathrm{NH_4OH}]} = \frac{K_w}{K_b}\frac{[\mathrm{NH_4^+}]}{[\mathrm{NH_4OH}]}$$

Taking log on both sides, we get
$$\log[\mathrm{H^+}] = \log K_w - \log K_b + \log\frac{[\mathrm{Salt}]}{[\mathrm{Base}]}$$

or $$-\text{pH} = -\text{p}K_\text{w} + \text{p}K_\text{b} + \log\frac{[\text{Salt}]}{[\text{Base}]} \Rightarrow \text{p}K_\text{w} - \text{pH} = \text{p}K_\text{b} + \log\frac{[\text{Salt}]}{[\text{Base}]}$$

$$\text{pOH} = \text{p}K_\text{b} + \log\frac{[\text{Salt}]}{[\text{Base}]} \qquad (10.24)$$

Substituting the concentrations in Eq. (10.22) in terms of C and h from the reaction

$$\begin{array}{llll}\text{NH}_4^+(\text{aq}) + \text{H}_2\text{O(l)} & \rightleftharpoons & \text{NH}_4\text{OH(aq)} & + \text{H}^+ \\ C(1-h) & & Ch & Ch\end{array}$$

we get $$K_\text{h} = \frac{Ch \times Ch}{C(1-h)} = \frac{Ch^2}{1-h}$$

As $h \ll 1$, we have $$Ch^2 = \frac{K_\text{w}}{K_\text{b}} \Rightarrow h = \sqrt{\frac{K_\text{w}}{K_\text{b}C}}$$

Now, $$[\text{H}^+] = Ch = C \times \sqrt{\frac{K_\text{w}}{K_\text{b}C}} = \sqrt{\frac{K_\text{w}C}{K_\text{b}}}$$

Taking log on both sides, we get

$$\log[\text{H}^+] = \frac{1}{2}\log K_\text{w} + \frac{1}{2}\log C - \frac{1}{2}\log K_\text{b}$$

$$\text{pH} = \frac{1}{2}\text{p}K_\text{w} - \frac{1}{2}\log C - \frac{1}{2}\text{p}K_\text{b}$$

or $$\text{pH} = 7 - \frac{1}{2}\log C - \frac{1}{2}\text{p}K_\text{b} \qquad (10.25)$$

Salt of Weak Acid and Weak Base

Consider the example of CH_3COONH_4, which is a salt of a weak acid (CH_3COOH) and a weak base (NH_4OH). The salt will be partially dissociated in aqueous medium.

$$\text{CH}_3\text{COONH}_4(\text{aq}) \rightarrow \text{NH}_4^+(\text{aq}) + \text{CH}_3\text{COO}^-(\text{aq})$$

The ions formed will go hydrolysis as follows:

$$\text{NH}_4^+(\text{aq}) + \text{CH}_3\text{COO}^-(\text{aq}) + \text{H}_2\text{O(l)} \rightleftharpoons \text{CH}_3\text{COOH} + \text{NH}_4\text{OH}$$

Acetic acid and ammonium hydroxide being a weak acid and base, respectively, will also exist in solution in partly dissociated form.

$$\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$$
$$\text{NH}_4\text{OH} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$$

The hydrolysis constant is K_h expressed as

$$K_\text{h} = \frac{[\text{NH}_4\text{OH}][\text{CH}_3\text{COOH}]}{[\text{NH}_4^+][\text{CH}_3\text{COO}^-]} \qquad (10.26)$$

We know that $K_\text{w} = [\text{H}^+]\,[\text{OH}^-]$ and $K_\text{a} = \dfrac{[\text{CH}_3\text{COO}^-]\times[\text{H}^+]}{[\text{CH}_3\text{COOH}]}$, $K_\text{b} = \dfrac{[\text{NH}_4^+]\times[\text{OH}^-]}{[\text{NH}_4\text{OH}]}$.

Comparing with the above equation, we get

$$K_h = \frac{K_w}{K_a K_b} \tag{10.27}$$

Substituting the concentrations in Eq. (10.26) in terms of C and α from the reaction

$$\underset{C(1-h)}{NH_4^+(aq)} + \underset{C(1-h)}{CH_3COO^-(aq)} + H_2O(l) \rightleftharpoons \underset{Ch}{CH_3COOH} + \underset{Ch}{NH_4OH}$$

we get
$$K_h = \frac{Ch \times Ch}{C^2(1-h)^2} = \frac{h^2}{(1-h)^2}$$

As $h \ll 1$, we have
$$h^2 = \frac{K_w}{K_a K_b} \Rightarrow h = \sqrt{\frac{K_w}{K_a K_b}}$$

Now, due to common ion effect, the acetate ion coming from CH_3COOH can be neglected, thus from the following reaction,

$$\underset{Ch}{CH_3COOH} \rightleftharpoons \underset{C(1-h)}{CH_3COO^-} + H^+$$

we have,
$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{C(1-h)[H^+]}{Ch}$$

As $h \ll 1$, we have
$$K_a = \frac{[H^+]}{h} \Rightarrow [H^+] = K_a h = K_a \times \sqrt{\frac{K_w}{K_a K_b}} = \sqrt{\frac{K_a K_w}{K_b}}$$

This expression is independent of the concentration of the salt.

1. if $K_a = K_b$, pH = 7 solution will be neutral.
2. if $K_a > K_b$, pH < 7 acidic solution.
3. if $K_a < K_b$, then pH > 7 alkaline solution.

Taking log on both sides, we get

$$\log[H^+] = \frac{1}{2}\log K_w + \frac{1}{2}\log K_a - \frac{1}{2}\log K_b$$
$$-pH = -\frac{1}{2}pK_w - \frac{1}{2}\log K_a + \frac{1}{2}pK_b$$

or
$$pH = 7 + \frac{1}{2}\log K_a - \frac{1}{2}pK_b \tag{10.28}$$

The degree of hydrolysis is independent of concentration of the solution and pH of such solutions can be determined by the above relation. The pH of the resulting solution will be determined by the relative strength of acid and base of which the cation and anion are a part.

Note: In case of weak base NH_4CN and weak acid CH_3COONH_4, both the ions are hydrolyzed with equal extent of hydrolysis for both cation and anion if $K_a \cong K_b$. In case $K_a < K_b$, it is expected that hydrolysis of CN^- ions is to a greater extent. However, the hydrolysis of CN^- ions takes place as follows:

$$CN^- + H_2O \rightleftharpoons HCN + OH^-$$

The OH^- ions produced react with NH_4^+ ions as follows:

$$OH^-(aq) + NH_4^+(aq) \rightleftharpoons NH_4OH$$

The production of OH^- from the former reaction will displace the above reaction to the right, so as to remove OH^- ions. So, the hydrolysis of one ion causes the other ion to be hydrolyzed as well to almost the same extent. So, we can assume that $[HCN] = [NH_4OH]$ even if $K_a \neq K_b$.

Salts of Weak Polyprotic Acids

Consider the following salts of weak polyprotic acids: Na_3PO_4, Na_2HPO_4 and NaH_2PO_4, each with concentration C. Given that for H_3PO_4, $K_{a1} \gg K_{a2} \gg K_{a3}$. To calculate the pH when Na_3PO_4 is hydrolyzed, we can say that only PO_4^{3-} is hydrolyzed. Then steps in hydrolysis are:

$$PO_4^{3-} + H_2O \rightleftharpoons HPO_4^{2-} + OH^- \quad K_{H1} = \frac{K_w}{K_{a3}}$$

$$HPO_4^{2-} + H_2O \rightleftharpoons H_2PO_4^- + OH^- \quad K_{H2} = \frac{K_w}{K_{a2}}$$

$$H_2PO_4^- + H_2O \rightleftharpoons H_3PO_4 + OH^- \quad K_{H3} = \frac{K_w}{K_{a1}}$$

Also,

$$\begin{aligned} H_3PO_4 &\rightleftharpoons H^+ + H_2PO_4^- && (K_{a1}) \\ H_2PO_4^- &\rightleftharpoons H^+ + HPO_4^{2-} && (K_{a2}) \\ HPO_4^{2-} &\rightleftharpoons H^+ + PO_4^{3-} && (K_{a3}) \end{aligned}$$

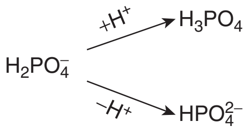
Since $K_{a1} \gg K_{a2} \gg K_{a3}$, therefore, $K_{H1} \gg K_{H2} \gg K_{H3}$.

Thus, we can consider the first step of hydrolysis only. Then,

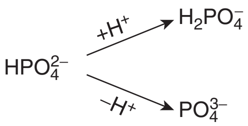
$$pH = \frac{1}{2}[pK_w + pK_{a3} + \log C]$$

pH Calculation of Amphoteric and Amphiprotic Ions

Similarly, in Na_2HPO_4 and NaH_2PO_4, the ions hydrolyzed are $H_2PO_4^-$ and HPO_4^{2-}, respectively. Both of these are amphiprotic ions. For calculation of pH of amphoteric or amphiprotic ions, consider the following example.



$$pH = \frac{1}{2}(pK_{a1} + pK_{a2})$$



$$pH = \frac{1}{2}(pK_{a2} + pK_{a3})$$

Therefore, pH of $Na_2HPO_4 = \frac{1}{2}(pK_{a2} + pK_{a3})$ and pH of $NaH_2PO_4 = \frac{1}{2}(pK_{a1} + pK_{a2})$.

Solved Example 10-24

The degree of hydrolysis and pH of 0.2 M solution of NH_4Cl will be [Given K_b for NH_4OH is 1.8×10^{-5}]

Solution

The reaction can be represented as

$$NH_4Cl + H_2O \rightleftharpoons H^+(aq) + CH_3COOH^-(aq)$$

	NH_4Cl	$H^+(aq)$	$CH_3COOH^-(aq)$
Before hydrolysis	C	0	0
After hydrolysis	$C(1-h)$	x	x

where h is the degree of hydrolysis.

$$h = \left(\frac{K_h}{C}\right) = \sqrt{\left(\frac{K_w}{K_b C}\right)} = \sqrt{\frac{10^{-14}}{1.8\times10^{-5}\times0.2}} = 5.27\times10^{-5}$$

From HCl, a strong acid, we have

$$[H^+] = Ch = C\sqrt{\left(\frac{K_h}{C}\right)} = \sqrt{(K_H C)}$$

$$= \sqrt{\left(\frac{K_w}{K_b}C\right)} = \sqrt{\left(\frac{10^{-14}\times0.2}{1.8\times10^{-5}}\right)} = 1.054\times10^{-5}$$

Therefore, $pH = -\log[H^+] = -\log(1.054\times10^{-5}) = 4.9771$

Solved Example 10-25

What is the percentage hydrolysis in 0.0003 M aqueous solution of NaOCN [K_a for HOCN $= 3.33 \times 10^{-4}$]?

Solution

The reaction involved is

$$NaOCN + H_2O \rightleftharpoons NaOH + HCN$$

The degree of hydrolysis is

$$h = \sqrt{\left(\frac{K_h}{C}\right)} = \sqrt{\left(\frac{K_w}{K_a C}\right)} = \sqrt{\frac{10^{-14}}{3.33\times10^{-4}\times0.003}} = 10^{-4}$$

Therefore,

$$\%\ \text{hydrolysis} = 10^{-4}\times100 = 10^{-2}$$

Solved Example 10-26

What is the pH of a 0.05 M aqueous NaCN solution [pK_b for $CN^- = 4.70$]?

Solution

The pK_a for HCN $= 14 - pK_b = 14 - 4.70 = 9.30$. Now,

$$pOH = \frac{1}{2}[pK_w - \log C - pK_a]$$

$$= \frac{1}{2}[14 - \log 0.5 - 9.30]$$

$$= \frac{1}{2}[14 + 0.3010 - 9.30] = 2.5$$

Therefore, $pH = 14 - 2.5 = 11.5$

Solved Example 10-27

What is the pH of mixture obtained by mixing 50 ml of 0.05 M NH_4OH and 50 mL of 0.05 M CH_3COOH [$K_a = 1.8 \times 10^{-5}$ and $K_b = 1.8 \times 10^{-5}$]?

Solution

The reaction involved is

$$NH_4OH + CH_3COOH \rightleftharpoons CH_3COONH_4 + H_2O$$

	NH_4OH	CH_3COOH	CH_3COONH_4	H_2O
Before hydrolysis	2.5	2.5	0	0
After hydrolysis	0	0	2.5	2.5

In this case, pH is decided on the basis of hydrolysis of salt.

$$[CH_3COONH_4] = \frac{2.5}{100} = 2.5\times10^{-2}\,M$$

Therefore,

$$pH = +\frac{1}{2}[\log K_b - \log K_w - \log K_a]$$

$$= \frac{1}{2}[pK_w + pK_a - pK_b]$$

$$= \frac{1}{2}[\log\ (1.8\times10^{-5}) + \log 10^{-14} - \log(1.8\times10^{-5})]$$

$$= 7$$

10.13 | BUFFER SOLUTIONS

Many chemical and biological systems are quite sensitive to pH. For example, if the pH of our blood were to change from the range of 7.35 to 7.42, either to 7.00 or to 8.00, we would die. Thus, a change in pH can produce unwanted effects, and systems that are sensitive to pH must be protected from the H^+ or OH^- that might be formed or consumed by some reaction. The solution containing solutes is said to be buffered or it is described as a buffer solution.

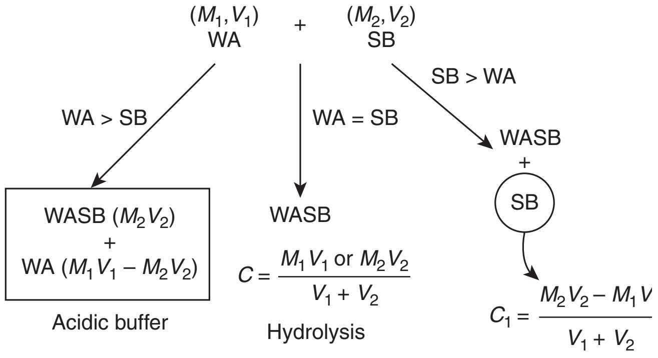
A **buffer** contains solutes that enable it to resist large changes in pH when small amounts of either strong acid or strong base are added to it. Ordinarily, the buffer consists of two solutes, one providing a weak Brönsted acid and the other a weak Brönsted base. Usually, the acid and base represent a conjugate pair. If the acid is molecular, then the conjugate base is *supplied by a soluble salt of the acid.* For example, a common buffer system consists of acetic acid plus sodium acetate, with the salt's acetate ion serving as the Brönsted base. In our blood, carbonic acid (H_2CO_3, a weak diprotic acid) and the bicarbonate ion (HCO_3^-, its conjugate base) serve as one of the buffer systems used to maintain a remarkably constant pH in the face of the body's production of organic acids by metabolism. Another common buffer consists of the weakly acidic cation, NH_4^+, supplied by a salt-like NH_4Cl, and its conjugate base, NH_3.

One important point about buffers is the distinction between keeping a solution at a particular pH and keeping it neutral – at a pH of 7. Although it is certainly possible to prepare a buffer to work at pH 7, buffers can be made that will work around any pH value throughout the pH scale.

Identification of Buffer

For identification of buffer, consider the following cases.

Case 1: Given a weak acid (WA) and a strong base (SB), with molar concentration and volume as M_1,V_1 and M_2,V_2 respectively. Then



Then pH values for the three conditions are, respectively

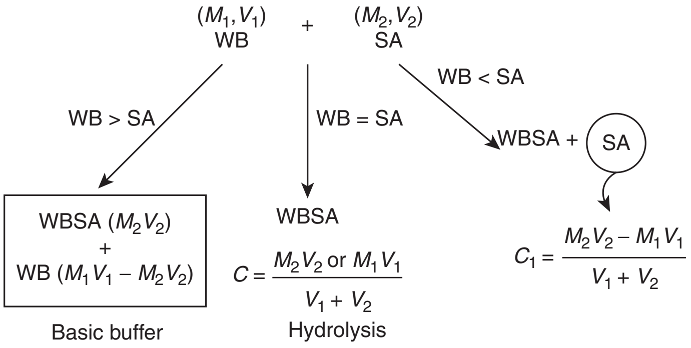
$$\text{pH} = \text{p}K_a + \log\left(\frac{M_2V_2}{M_1V_1 - M_2V_2}\right) \quad \text{(Acidic buffer)}$$

$$\text{pH} = \frac{1}{2}(\text{p}K_w + \text{p}K_a + \log C) \quad \text{(Hydrolysis)}$$

and

$$\text{pH} = 14 + \log C_1$$

Case 2: Given a weak base (WB) and a strong acid (SA), with molar concentration and volume as M_1,V_1 and M_2,V_2 respectively. Then



Then pH values for the three conditions are, respectively

$$\text{pOH} = \text{p}K_b + \log\left(\frac{M_2V_2}{M_1V_1 - M_2V_2}\right) \qquad \text{(Basic buffer)}$$

$$\text{pH} = \frac{1}{2}(\text{p}K_w - \text{p}K_b - \log C) \qquad \text{(Hydrolysis)}$$

and

$$\text{pH} = -\log C_1$$

pH of Buffer Solutions: Henderson–Hasselbalch Equation

We have seen that important buffers generally consist of mixtures of weak acids and their salts or weak bases and their salts and are known as **acidic buffers** and **basic buffers**, respectively. If the pH of the buffer solution is less than 7, it is called an acidic buffer and if the pH of the solution is more than 7, it is called a basic buffer. Let us now understand how the pH of acidic and basic buffers are determined and their buffer action.

pH of an Acidic Buffer

A common acidic buffer is a mixture of acetic acid and sodium acetate. The salt sodium acetate is completely dissociated in aqueous medium while acetic acid being a weak acid is partly dissociated. At equilibrium,

$$CH_3COOH \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$$

The acid dissociation constant can be expressed as

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

or

$$[H^+] = K_a\frac{[CH_3COOH]}{[CH_3COO^-]}$$

Taking negative logarithm on both sides, we get

$$-\log[H^+] = -\log K_a - \log\frac{[CH_3COOH]}{[CH_3COO^-]}$$

$$\text{pH} = \text{p}K_a - \log\frac{[CH_3COOH]}{[CH_3COO^-]} = \text{p}K_a + \log\frac{[CH_3COO^-]}{[CH_3COOH]}$$

In general, for an acid HA, the equation can be expressed as

$$\text{pH} = \text{p}K_a + \log\frac{[A^-]}{[HA]}$$

In most buffers used, the anion A^- comes from a salt in which the cation has a charge of 1^+ such as NaA, and the acid is monoprotic. With these as conditions, the equation is sometimes written as

$$\text{pH} = \text{p}K_a + \log\frac{[\text{Salt}]}{[\text{Acid}]} \qquad (10.29)$$

The relation is called **Henderson–Hasselbalch equation**, and it shows that the pH of an acidic buffer (mixture of weak acid and its salt) depends on the pK_a of the acid and the concentrations of the salt and acid in the mixture.

On large dilution, the Henderson- Hasselbalch equation may not hold. For example, in the above case, if the solution is diluted 1000 times, then CH_3COOH is no longer a weak electrolyte. Given that concentration of CH_3COOH and CH_3COONa is C_1 and C_2, respectively and equilibrium constant for acetic acid is K_a. Then for CH_3COOH

$$\begin{array}{llll} & H_3CCOOH & \rightleftharpoons CH_3COO^- & + H^+ \\ \text{At } t=0 & C_1 & 0 & 0 \\ \text{At } t=t_{eq} & C_1-x & x+C_2 & x \end{array}$$

Similarly, for CH_3COONa

$$\begin{array}{llll} & H_3CCOO^-Na^+ & \rightleftharpoons CH_3COO^- & + Na^+ \\ \text{At } t=0 & C_2 & 0 & 0 \\ \text{At } t=t_{eq} & 0 & C_2+x & C_2 \end{array}$$

Therefore,

$$K_a = \frac{x(x+C_2)}{C_1-x}$$

Solving for x, we get

$$pH = -\log[H^+] = -\log x$$

Buffer Action of Acidic Buffer

To work, a buffer must be able to neutralize either a strong acid or strong base that is added to it. This is precisely what the weak base and weak acid components of the buffer do. Consider, for example, a buffer composed of acetic acid, CH_3COOH, and acetate ion, CH_3COO^-, supplied by a salt such as CH_3COONa. If we add extra H^+ to the buffer (from a strong acid) the acetate ion (the weak conjugate base) can react with it as follows.

$$H^+(aq) + CH_3COO^-(aq) \rightarrow CH_3COOH(aq)$$

Thus, the added H^+ changes some of the buffer's Brönsted base, CH_3COO^-, to its conjugate (weak) acid, CH_3COOH. This reaction prevents a large buildup of H^+ that would otherwise be caused by the addition of the strong acid. A similar response occurs when a strong base is added to the buffer. The OH^- from the strong base will react with some CH_3COOH.

$$CH_3COOH(aq) + OH^-(aq) \rightarrow CH_3COO^-(aq) + H_2O(aq)$$

Here the added OH^- changes some of the buffer's Brönsted acid, CH_3COOH, into its conjugate base, CH_3COO^-. This prevents a buildup of OH^-, which would otherwise cause a large change in the pH. Thus, one member of a buffer team neutralizes H^+ that might get into the solution, and the other member neutralizes OH^-.

pH of a Basic Buffer

A common example of a basic buffer is a mixture of ammonium hydroxide and ammonium chloride. The salt ammonium chloride is completely dissociated in aqueous solution, while ammonium hydroxide being a weak base is slightly dissociated, so the equilibrium mixture contains ammonium hydroxide as well as ammonium and chloride ions.

At equilibrium,

$$NH_4OH(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

$$NH_4Cl(s) \rightleftharpoons NH_4^+(aq) + Cl^-(aq)$$

The base dissociation constant can be expressed as

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]}$$

or
$$[\text{OH}^-] = K_b \frac{[\text{NH}_4\text{OH}]}{[\text{NH}_4^+]}$$

Taking negative logarithm on both sides, we get

$$-\log[\text{OH}^-] = -\log K_b - \log\frac{[\text{NH}_4\text{OH}]}{[\text{NH}_4^+]}$$
$$\text{pOH} = \text{p}K_b - \log\frac{[\text{NH}_4\text{OH}]}{[\text{NH}_4^+]} = \text{p}K_b + \log\frac{[\text{NH}_4^+]}{[\text{NH}_4\text{OH}]}$$

In general, for a base HB, the equation can be expressed as

$$\text{pOH} = \text{p}K_b + \log\frac{[\text{Salt}]}{[\text{Base}]} \tag{10.30}$$

Here we assume that the concentration of ammonium ions is same as the concentration of the salt because the ammonium ions from ammonium hydroxide are negligible. The ionization of ammonium hydroxide is further suppressed by the presence of ammonium ions from the salt. Equation (10.30) is also called **Henderson–Hasselblach equation**.

If pOH of an aqueous solution is known, the pH can be calculated as follows. We know that pH + pOH = 14. Substituting in Eq. (10.30), we get

$$\text{pH} = 14 - \text{p}K_b - \log\frac{[\text{Salt}]}{[\text{Base}]} = \text{p}K_a + \log\frac{[\text{Base}]}{[\text{Salt}]} \quad (\text{as } \text{p}K_a + \text{p}K_b = 14)$$

Buffer Action of Basic Buffer

To work properly, a basic buffer must be able to neutralize either a strong acid or strong base that is added to it. Consider, for example, a basic buffer composed of ammonium hydroxide and ammonium ions supplied by salt such as ammonium chloride. If we add extra H^+ to the buffer from a strong acid such as HCl, they will combine with OH^- ions in the solution to form water.

$$\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightleftharpoons \text{H}_2\text{O(l)}$$

Thus, addition of H^+ ions does not affect the pH of the solution. Next let us understand what happens if we add extra OH^- ions to the buffer from a strong base such as NaOH. These ions will react with ammonium ions present in the solution due to slight ionization of NH_4OH.

$$\text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{NH}_4\text{OH(aq)}$$

Hence, the addition of a base to the buffer solution also does not alter the pH of the solution.

Salt Buffer

When a solution of a salt itself acts as a buffer, it is known as a salt buffer. These are salts of a weak acid and weak base.

For example,
$$\text{CH}_3\text{COONH}_4 \rightleftharpoons \text{CH}_3\text{COO}^- + \text{NH}_4^+$$

An acid added reacts with CH_3COO^- to produce CH_3COOH, while a base added reacts with NH_4^+ to produce NH_4OH.

Buffer Capacity

Buffer capacity, also known as **buffer index**, is the change in the concentration of buffer acid (or base) required to change the pH of its solution by one, while keeping the concentration of [salt] + [acid] or [salt] + [base] constant.

Let there be an acidic buffer containing a moles of acid (HA), b moles of salt (NaA) and K_a of acid is given, then we have $(\text{pH})_1$ as

$$(\text{pH})_1 = \text{p}K_a + \log\frac{b}{a}$$

Let us add a very small amount of strong base, that is, x moles, such that $x \ll a$ and $x \ll b$

$$(\text{pH})_2 = \text{p}K_\text{a} + \log\frac{b+x}{a-x}$$

$$\Delta\text{pH} = (\text{pH})_2 - (\text{pH})_1 = \log\left(\frac{b+x}{a-x}\right) - \log\left(\frac{b}{a}\right)$$

$$\Delta\text{pH} = \log\left(\frac{(b+x)}{b}\frac{a}{(a-x)}\right)$$

$$= \frac{1}{2.303}\ln\left(\frac{(b+x)}{b}\frac{a}{(a-x)}\right)$$

Differentiating the above equation with respect to x keeping y constant, we get

$$\frac{\partial(\text{pH})}{\partial x} = \frac{1}{2.303}\frac{b(a-x)}{a(b+x)}\left(\frac{a}{b}\frac{(a-x)(1)-(b+x)(-1)}{(a-x)^2}\right)$$

$$\frac{\partial(\text{pH})}{\partial x} = \frac{1}{2.303}\frac{(a+b-2x)}{(a-x)(b+x)}$$

$$\frac{\partial x}{\partial(\text{pH})} = \frac{2.303(a-x)(b+x)}{(a+b-2x)} = \text{Buffer index (B.I.)}$$

Since, $x \ll a$ and $x \ll b$, therefore,

$$\frac{\partial x}{\partial(\text{pH})} = \frac{2.303(ab)}{(a+b)} = \text{Buffer index or Buffer capacity}$$

If we take the total amount of acid + salt, that is, $a + b = y$, Then

$$\text{B.I.} = \frac{\partial b}{\partial(\text{pH})} = \frac{2.303(y-b)b}{y}$$

To get maximum buffer capacity, $\dfrac{\partial}{\partial b}(\text{B.I.}) = 0$

$$\frac{2.303}{y}(y-2b) = 0 \Rightarrow b = \frac{y}{2}.$$

Therefore, $b = \dfrac{y}{2}$ and $a = b = \dfrac{y}{2}$

Hence, for maximum buffer capacity, moles of WA = moles of WASB (salt)

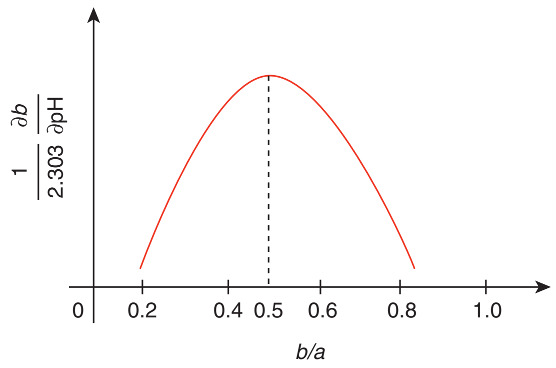


Figure 10.3 Buffer capacity.

Buffer Range

The range of buffer within which a buffer can be used is difficult to predict. Therefore, it is generally accepted that a solution has useful buffer index provided that the value of [Salt]/[Acid] or [Salt]/[Base] lies within the range 10–0.1. Hence, from Henderson equation we have

$$\mathrm{p}K_\mathrm{a} + \log(0.1) < \mathrm{pH} < \mathrm{p}K_\mathrm{a} + \log 10$$

or

$$(\mathrm{p}K_\mathrm{a} - 1) < \mathrm{pH} < (\mathrm{p}K_\mathrm{a} + 1)$$

Beyond this range, the buffer index is very small for any practical application.

Solved Example 10-28

The pH of buffer changes from 4.745 to 4.832 when 0.01 mol of KOH is added to 0.5 L of buffer. What is the buffer index?

Solution

The buffer index is

$$\text{B.I.} = \frac{\text{Moles of Acid/Base add to 1 L of buffer}}{\text{Change in pH Value}}$$

$$= \frac{0.01 \times 2}{4.832 - 4.745}$$

$$= 0.23$$

Solved Example 10-29

20 mL of 0.2 M NaOH is added of 50 mL of 0.2 M acetic acid to give 70 mL of the solution. What is the pH of the solution? (The ionization constant of acetic acid is 1.8×10^{-5}).

Solution

The addition of NaOH converts equivalent amount of acetic acid into sodium acetate. Hence, concentration of acetic acid after the addition of sodium hydroxide $= \frac{30}{70} \times 0.2$ M

Concentration of sodium acetate after the addition of sodium hydroxide $= \frac{20}{70} \times 0.2$ M

Hence, using the expression $\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\frac{[\text{Salt}]}{[\text{Acid}]}$, we get

$$\mathrm{pH} = -\log(1.8 \times 10^{-5}) + \log\left(\frac{20}{30}\right) = 4.745 - 0.177 = 4.568$$

Solved Example 10-30

To study the effects of a weakly acidic medium on the rate of corrosion of a metal alloy, a student prepared a buffer solution containing both 0.11 M CH_3COONa and 0.090 M CH_3COOH. What is the pH of the solution?

Solution

The buffer solution contains *both* the weak acid CH_3COOH and its conjugate base CH_3COO^-. Earlier we noted that when both solute species are present we can use *either* K_a or K_b to perform calculations, whichever is handy. In our tables we find $K_\mathrm{a} = 1.8 \times 10^{-5}$ for CH_3COOH, so the simplest approach is to use the equation for the ionization of the acid. We will also be able to use the simplifying approximations developed earlier; these always work for buffers.

As usual, we begin with the chemical equation and the expression for K_a.

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$$

$$K_\mathrm{a} = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = 1.8 \times 10^{-5}$$

Let us set up the concentration table so we can proceed carefully. We will take the initial concentrations of CH_3COOH and CH_3COO^- to be the values given in the problem statement. There's no H^+ present from a strong acid, so we set that concentration equal to zero. If the initial concentration of H^+ is zero, its concentration must increase on the way to equilibrium, so under H^+ in the change row we enter $+x$. The other changes follow from that. Here is the representation.

	$CH_3COOH \rightleftharpoons$	$H^+ +$	CH_3COO^-
Initial concentration	0.090	0	0
Changes in concentration	$-x$	x	x
Equilibrium concentration	$(0.090 - x)$ ≈ 0.090	x	$(0.11 + x)$ ≈ 0.11

For buffer solutions the quantity x will be very small, so it is safe to make the simplifying approximations. What remains, then, is to substitute the quantities from the last row of the table into the K_a expression.

$$\frac{(x)(0.11+x)}{(0.090-x)} \approx \frac{(x)(0.11)}{(0.090)} = 1.8\times10^{-5}$$

Solving for x gives us $x = \dfrac{(0.090)\times1.8\times10^{-5}}{(0.11)} = 1.5\times10^{-5}$

Because x equals $[H^+]$, we now have $[H^+] = 1.5\times10^{-5}$ M. Then we calculate pH:

$$\text{pH} = -\log(1.5\times10^{-5}) = 4.82$$

Thus, the pH of the buffer is 4.82.

Solved Example 10-31

What is the pH of a buffer solution prepared by 30 g of Na_2CO_3 in 1000 mL and 150 mL of M HCl. [K_a for $HCO_3^- = 5.63\times10^{-11}$]?

Solution

The reaction is represented as

	Na_2CO_3 +	$HCl \rightleftharpoons$	$NaCl +$	$NaHCO_3$
Milliequiv. before reaction	$\frac{30}{106}\times100$ $= 283$	150×1 $= 150$	0	0
Milliequiv. after reaction	133	0	150	150

The solution contains Na_2CO_3 and HCO_3^- and thus, acts as buffer. The pH is

$$\text{pH} = -\log K_a + \log\frac{[CO_3^{2-}]}{[HCO_3^-]} = -\log(5.63\times10^{-11}) + \log\frac{133}{150}$$
$$= 10.249 - 0.052 = 10.197$$

Solved Example 10-32

What is the amount of $(NH_4)_2SO_4$ in grams that must be added to 500 mL of 0.2 M NH_3 to yield a solution of pH = 9.35. (K_b for $NH_3 = 1.78\times10^{-5}$)?

Solution

The pOH can be determined as

$$\text{pOH} = -\log K_b + \log\frac{[\text{Salt}]}{[\text{Base}]} = -\log K_b + \log\frac{[NH_4^+]}{[NH_4OH]} \quad (1)$$

as NH_4^+ is obtained from $(NH_4)_2SO_4$. The values of pH = 9.35, so pOH = 14 − 9.35 = 4.65.

Now, millimoles of NH_4OH in solution = 0.2 × 500 = 100

Let the millimoles of NH_4^+ added in solution = x. Then, we have $[NH_4^+] = x/500$ and $[NH_4OH] = 100/500 = 1/5$. Substituting in Eq. (1), we get

$$4.65 = -\log(1.78\times10^{-5}) + \log\frac{x/500}{1/5}\; 4.65 = 4.7496 + \log\frac{x}{100}$$

Solving, we get $x = 79.51$. Now, the millimoles of $(NH_4)_2SO_4$ added $= \dfrac{x}{2} = \dfrac{79.51}{2} = 39.755$

Therefore,

$$\frac{w_{(NH_4)_2SO_4}}{132}\times1000 = 39.755 \Rightarrow w_{(NH_4)_2SO_4} = 5.248\text{ g}$$

Solved Example 10-33

What volume of 0.1 M sodium formate solution should be added to 50 mL of 0.05 M formic acid to produce a buffer solution of pH = 4.0 (pK_a of formic acid = 3.80)?

Solution

Suppose V mL of 0.1 M HCOONa be mixed to 50 mL of 0.05 M HCOOH, then

$$[\text{HCOONa}] = \frac{0.1 \times V}{(V+50)} \text{ and } [\text{HCOOH}] = \frac{50 \times 0.05}{V+50}$$

Now, pH is given by

$$\text{pH} = -\log K_b + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

or $$4.0 = 3.80 + \log \frac{(0.1 \times V)/(V + 50)}{2.5/(V+50)}$$

or $$4.0 - 3.8 = \log\ (0.1) + \log V - \log 2.5$$

or $$0.2 = -1 - \log V - 0.3979$$

or $$\log V = 1.5979 \Rightarrow V = 39.62 \text{ mL}$$

Solved Example 10-34

A certain buffer solution contains equal concentration of X^- and HX^- (K_b for X^- is 10^{-10}). What is the pH of the buffer?

Solution

Given that K_b for $X^- = 10^{-10}$. For conjugate acid–base pair, we have

$$K_{a(HX)} \times K_{b(X^{-1})} = 10^{-14} \Rightarrow K_{a(HX)} = \frac{10^{-14}}{10^{-10}} = 10^{-4}$$

But $[HX] = [X^-]$, so pH is

$$\text{pH} = -\log K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} = -\log 10^{-4} = 4$$

Solved Example 10-35

How much will the pH change if 0.020 mol of HCl is added to a buffer solution that was made by dissolving 0.12 mol of NH_3 and 0.095 mol of NH_4Cl in 250 mL of water?

Solution

The reaction is $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$ with

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5}$$

The solution contains 0.12 mol of NH_3 and 0.095 mol of NH_4^+ from the complete dissociation of the salt NH_4Cl. Substituting these values in mass action expression, we get.

$$1.8 \times 10^{-5} = \frac{\text{mol } NH_4^+ \times [OH^-]}{\text{mol } NH_3} = \frac{(0.095)[OH^-]}{0.12} \quad (1)$$

which gives $[OH^-]$ gives 2.3×10^{-5} M. The pH is calculated from pOH value

$$\text{pOH} = -\log(2.3 \times 10^{-5}) = 4.64$$
$$\text{pH} = 14.00 - 4.64 = 9.36$$

This is the pH before we add any HCl. Now, consider the reaction taking place when we add the HCl to the buffer. The 0.020 mol of HCl is completely ionized, so we add 0.020 mol H^+ to react as:

$$NH_3(aq) + H^+(aq) \rightarrow NH_4^+(aq)$$

0.020 mol of H^+ reacts with 0.020 mol of NH_3 to form 0.020 mol of NH_4^+, thus decreasing the number of moles of NH_3 by 0.020 mol and increasing the number of moles of NH_4^+ by 0.020 mol.

Equation (1) is modified accordingly with these new values to obtain

$$1.8 \times 10^{-5} = \frac{(0.115)[OH^-]}{0.10}$$

which gives $[OH^-]$ as 1.6×10^{-5} M. The pH is calculated from pOH value

$$\text{pOH} = -\log(1.6 \times 10^{-5}) = 4.80$$
$$\text{pH} = 14.00 - 4.80 = 9.20$$

This is the pH after addition of the acid. Therefore, the change in pH = 9.36 – 9.20 = 0.16.

Solved Example 10-36

One liter of buffer is made by dissolving 100.0 g of acetic acid, CH_3COOH, and 100.0 g of sodium acetate, CH_3COONa, in enough water to make one liter. What is the pH of the solution?

Solution

First, we find the concentrations of the acetic acid and the acetate ion:

$$[CH_3COOH] = (100.0\text{ g }CH_3COOH)\left(\frac{1}{60.053}\right)\left(\frac{1}{1}\right)$$
$$= 1.665\text{ M}$$

$$[CH_3COONa] = (100.0\text{ g }CH_3COOH)\left(\frac{1}{82.035}\right)\left(\frac{1}{1}\right)$$
$$= 1.219\text{ M}$$

The reaction can be represented as

	$CH_3COOH \rightleftharpoons$	$H^+ +$	CH_3COO^-
Initial concentration	1.665	0	1.219
Changes in concentration	$-x$	x	x
Equilibrium concentration	$(1.665-x)$	x	$(1.219+x)$

with ionization constant as

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} \Rightarrow 1.8\times10^{-5} = \frac{(1.219+x)(x)}{(1.665-x)}$$

Assume that x is small and solving for x, we get $x = 2.5\times10^{-5} = [H^+]$. So,

$$pH = -\log[H^+] = -\log(2.5\times10^{-5}) = 4.61$$

Solved Example 10-37

How much will the pH change if we add 0.15 mol NaOH to 1.00 L of a buffer that contains 1.00 mol CH_3COOH and 1.00 mol CH_3COONa?

Solution

The NaOH added to a buffer solution will react with the CH_3COOH as

$$NaOH + CH_3COOH \rightarrow CH_3COONa + H_2O$$

First, we calculate the amount of acid and base after the addition of the NaOH”

Moles of CH_3COONa = 1.00 mol CH_3COONa + 0.15 mol CH_3COONa = 1.15 mol

Moles of CH_3COOH = 1.00 mol CH_3COOH – 0.15 mol CH_3COONa = 0.85 mol

The concentration is $[CH_3COONa] = (1.15/1)$ M and $[CH_3COOH] = (0.85/1)$ M. Substituting these in the pH expression, we get

$$pH = pK_a + \log\frac{[\text{Salt}]}{[\text{Acid}]} = 4.74 + \log\frac{1.15}{0.85} = 4.87$$

The pH of the initial solution was 4.74 since the concentration of the acid equals the concentration of the salt. So, the pH change = 4.74 – 4.87 = 0.13

Solved Example 10-38

A buffer is prepared by mixing 50.0 g of NH_3 and 50.0 g of NH_4Cl in 500 mL of solution. What is the pH of this buffer and what will the pH change to if 5.00 g of HCl is then added to the mixture?

Solution

First, we calculate the moles of the salt and the acid, then calculate the pH of the solution.

$$\text{Moles of }NH_3 = (50.0\text{ g }NH_3)\left(\frac{1}{17.03}\right) = 2.94\text{ mol}$$

$$\text{Moles of }NH_4Cl = (50.0\text{ g }NH_4Cl)\left(\frac{1}{53.49}\right) = 0.935\text{ mol}$$

The reaction is $NH_4^+ \rightarrow NH_3 + H^+$ for which ionization constant is

$$K_a = \frac{K_w}{K_b} = \frac{1.0\times10^{-14}}{1.8\times10^{-5}} = 5.6\times10^{-10}$$

Now, $pK_a = -\log(K_a) = -\log(5.6\times10^{-10}) = 9.26$. Substituting values in the pH expression, we get

$$pH = pK_a + \log\frac{[\text{Salt}]}{[\text{Acid}]} = 9.26 + \log\frac{2.94}{0.935} = 9.76$$

If 5.00 g of HCl is add, the solution will become more acidic, the reaction then is $NH_3 + H^+ \rightarrow NH_4^+$

$$\text{Moles of HCl} = (5.00\text{ g HCl})\left(\frac{1}{36.46}\right) = 0.137\text{ mol}$$

The number of moles of NH_4^+ will increase by this amount and the number of moles of NH_3 will decrease by this amount.

$$\text{Moles of } NH_3 = 2.94\text{ mol } NH_3 - 0.137\text{ mol} = 2.80\text{ mol}$$
$$\text{Moles of } NH_4^+ = 0.935\text{ mol} + 0.137\text{ mol} = 1.07\text{ mol}$$

Substituting in pH expression, we get

$$\text{pH} = \text{p}K_a + \log\frac{[\text{Salt}]}{[\text{Acid}]} = 9.26 + \log\frac{2.80}{1.07} = 9.67$$

Solved Example 10-39

Two buffers (X) and (Y) of pH 4.0 and 6.0, respectively, are prepared from acid HA and the salt NaA. Both the buffers are 0.50 M in HA. What would be the pH of the solution obtained by mixing equal volumes of the two buffers? (Given that $K_{HA} = 1.0 \times 10^{-5}$.)

Solution

We know that $\text{pH} = \text{pK}_a + \log\frac{[\text{Salt}]}{[\text{Acid}]}$

For buffer X,

$$4 = 5 + \log\frac{[\text{Salt}]}{[0.5]} \Rightarrow \log\frac{[\text{Salt}]}{[0.5]} = -1$$

or $\quad \frac{[\text{Salt}]}{0.5} = 10^{-1}$

or $\quad [\text{Salt}] = 5 \times 10^{-2}\text{ M}$

For buffer Y,

or $\quad [6 = 5 + \log\frac{[\text{Salt}]}{[0.5]}$

or $\quad [\log\frac{[\text{Salt}]}{[0.5]} = 1 \Rightarrow \frac{[\text{Salt}]}{[0.5]} = 10$

or $\quad [\text{Salt}] = 5\text{ M}$

When equal volumes of both the buffers are mixed,

$$[\text{Acid}] = 0.5\text{ M and } [\text{Salt}] = \frac{5\times10^{-2}}{2} + \frac{5}{2} = 2.5025$$

So, the pH is

$$\text{pH} = \text{pK}_a + \log\frac{[\text{Salt}]}{[\text{Acid}]} = 5 + \log\frac{2.5025}{0.5}$$
$$= 5 + \log 5.05 = 5.7$$

10.14 | ACID–BASE TITRATIONS

In Chapter 2, we have learnt how acid-base titrations are important component of volumetric analysis and how the data from these titrations can be used in various stoichiometric calculations. In performing acid-base titration, the titration is halted at the **end point** when a change in color of an indicator occurs. Ideally, this end point should occur at the **equivalence point**, when stoichiometrically equivalent amounts of acid and base have combined. To obtain this ideal result, selecting an appropriate indicator requires foresight. We will understand this better by studying how the pH of the solution being titrated changes with the addition of titrant. When the pH of a solution at different stages of a titration is plotted against the volume of titrant added, we obtain a **titration curve**. The values of pH in these plots can be measured using a pH meter during the titration.

Strong Acid vs. Strong Base

The titration of HCl(aq) with a standardized NaOH solution illustrates the titration of a strong acid by a strong base. The molecular and net ionic equations are

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O$$
$$H^+(aq) + OH^-(aq) \rightarrow H_2O$$

Figure 10.4 shows the plot for titration of a strong acid with a strong base. From the figure:

In Zone 1 SB < SA ⇒ SASB + SA
In Zone 2 SB = SA ⇒ SASB
In Zone 3 SB > SA ⇒ SASB + SB

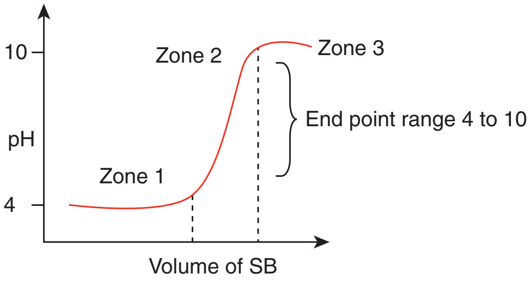


Figure 10.4 Titration curve for strong acid vs. strong base.

At the start, before any titrant has been added, the receiving flask contains only 0.2000 M HCl. Because this is a strong acid, we know that

$$[H^+] = [HCl] = 0.2000\ M$$

So the initial pH is

$$pH = -\log(0.2000) = 0.70$$

After the start but before the equivalence point we need to determine the concentration of the excess reactant in a simple limiting reactant problem. Let's first calculate the amount of HCl initially present in 25.00 mL of 0.2000 M HCl.

$$25.00\ \text{mL HCl soln} \times \frac{0.2000\ \text{mol HCl}}{1000\ \text{mL HCl soln}} = 5.000 \times 10^{-3}\ \text{mol HCl}$$

Now suppose we add 10.00 mL of 0.2000 M NaOH from the burette. The moles of NaOH added is

$$10.00\ \text{mL NaOH soln} \times \frac{0.2000\ \text{mol NaOH}}{1000\ \text{mL NaOH soln}} = 2.000 \times 10^{-3}\ \text{mol NaOH}$$

We can see that we have more moles of HCl than NaOH (and the mole ratio is 1:1) so that the base neutralizes 2.000×10^{-3} mol of HCl, and the amount of HCl remaining is

$$(5.000 \times 10^{-3} - 2.000 \times 10^{-3})\ \text{mol HCl} = 3.000 \times 10^{-3}\ \text{mol HCl remaining}$$

To obtain the concentration we divide by the total volume of the solution that is now (25.00 + 10.00) mL = 35.00 mL = 0.03500 L. The $[H^+]$ is

$$[H^+] = \frac{3.000 \times 10^{-3}\ \text{mol}}{0.03500\ \text{L}} = 8.571 \times 10^{-2}\ \text{M}$$

The corresponding pH is 1.07.

$$[H^+] = \frac{M_A V_A - M_B V_B}{V_A + V_B}$$

At the equivalence point, we can calculate the volume of NaOH added as

$$M_{HCl} \times V_{HCl} = M_{NaOH} \times V_{NaOH}$$

$$V_{NaOH}(\text{at equivalence point}) = \frac{(0.2000\ M_{HCl})(25.00\ \text{mL HCl})}{(0.2000\ \text{M NaOH})} = 25.00\ \text{mL}$$

At this point we have exactly neutralized all of the acid with base and neither HCl nor NaOH are in excess. The solution contains only NaCl and we have already observed that NaCl solutions are neutral with a pH = 7.00. The pH at the equivalence point of all strong acid–strong base titrations is 7.00.

After the equivalence point we will have an excess of base. As we did before, we calculate the moles of acid and the moles of base. Now the moles of base will be larger and we subtract the moles of acid to find the excess moles of base. This is divided by the total volume to obtain the $[OH^-]$ from which the pH is calculated. Here we follow how the pH changes during the titration of 25.00 mL of 0.2000 M HCl with 0.2000 M NaOH (Fig. 10.5).

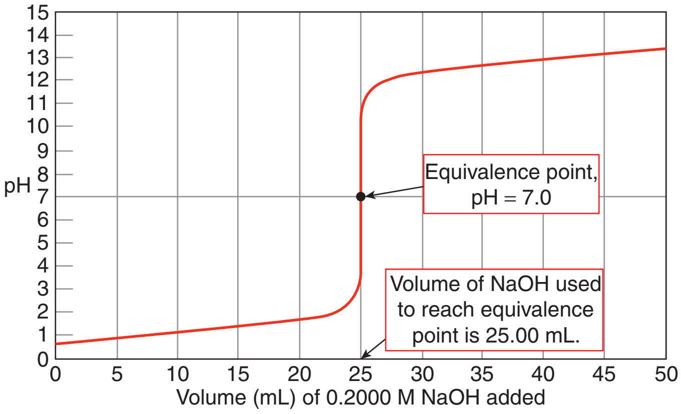


Figure 10.5 Titration curve for titrating a strong acid with a strong base.

Weak Acid vs. Strong Base

The calculations for the titration of a weak acid by a strong base are a bit more complex than when both the acid and base are strong. This is because we have to consider the equilibria involving the weak acid and its conjugate base. As an example, let's do the calculations and draw a titration curve for the titration of 25.00 mL of 0.2000 M CH_3COOH with 0.2000 M NaOH. The same four points are calculated but they use different equations.

The molecular and net ionic equations we will use are

$$CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + H_2O$$
$$CH_3COOH(aq) + OH^-(aq) \rightarrow CH_3COO^-(aq) + H_2O$$

Because the concentrations of both solutions are the same, and because the acid and base react in a one-to-one mole ratio, we know that we will need exactly 25.00 mL of the base to reach the equivalence point. With this as background, let us look at what is involved in calculating the pH at various points along the titration curve.

Figure 10.6 shows the plot for titration of a weak acid (WA) with a strong base (SB). From the figure:

In Zone 1 : WA > SB ⇒ WASB + WA (Acidic buffer)

Thus, the curve will be flatter in this zone, as it will resist change in pH.

In Zone 2: WA = SB ⇒WASB

In Zone 3: WA < SB ⇒ WASB + SB

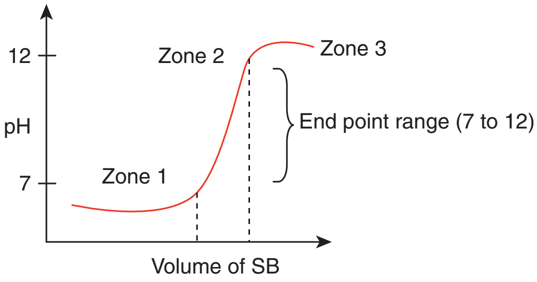


Figure 10.6 Titration curve for a weak acid vs. strong base.

At the start the solution is simply a solution of the weak acid CH_3COOH. We must use K_a to calculate the pH. We have seen that in many situations the simplifying assumptions hold and the calculations are summarized as

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = \frac{(x)(x)}{(0.2000 - x)} \approx \frac{(x)(x)}{0.2000} = 1.8 \times 10^{-5}$$
$$x^2 = 3.6 \times 10^{-6} \;\; \text{(rounded)} \Rightarrow x = [H^+] = 1.9 \times 10^{-3}$$

This result gives us a pH of 2.72. This is the pH before any NaOH is added.

Between the start and the equivalence point, as we add NaOH to the CH_3COOH, the chemical reaction produces CH_3COO^-, so the solution contains both CH_3COOH and CH_3COO^- (it is a buffer solution). Our equilibrium law can be rearranged to read

$$[H^+] = \frac{K_a[CH_3COOH]}{[CH_3COO^-]} = \frac{K_a(\text{mol } CH_3COOH)}{(\text{mol } CH_3COO^-)}$$

Now all we need to do is solve a limiting reactant calculation to determine the moles of acetic acid, CH_3COOH, left after each addition of NaOH and at the same time calculate the moles of acetate ion, CH_3COO^-, formed.

Let us see what happens when we add 10.00 mL of NaOH solution. The initial moles of acetic acid are

$$0.2000 \text{ M } CH_3COOH \times 0.02500 \text{ L} = 5.000 \times 10^{-3} \text{ mol}$$

The moles of NaOH added are $0.2000 \text{ M NaOH} \times 0.01000 \text{ L} = 2.000 \times 10^{-3} \text{ mol}$.

The moles of acetic acid left are $5.000 \times 10^{-3} \text{ mol} - 2.000 \times 10^{-3} \text{ mol} = 3.000 \times 10^{-3} \text{ mol}$

From the chemical equations above, the moles of NaOH added are stoichiometrically equal to the moles of acetate ion formed. We therefore have 2.000×10^{-3} mol CH_3COO^-. Entering the values for the K_a and the moles of acetic acid and acetate ions we get

$$[H^+] = \frac{(1.8 \times 10^{-5})(3.000 \times 10^{-3} \text{ mol } CH_3COOH_2)}{(2.000 \times 10^{-3} \text{ mol } CH_3COO^-)} = 2.7 \times 10^{-5} \text{ M}$$

and the pH is 4.57.

$$[H^+] = K_a \frac{M_A V_A - M_B V_B}{V_A + V_B}$$

At the equivalence point, all the CH_3COOH has reacted and the solution contains the salt CH_3COONa (i.e., we have a mixture of the ions Na^+ and CH_3COO^-).

We began with 5.000×10^{-3} mol of CH_3COOH, so we now have 5.000×10^{-3} mol of CH_3COO^- (in 0.05000 L). The concentration of CH_3COO^- is

$$[CH_3COO^-] = \frac{5.000 \times 10^{-3}\ \text{mol}}{0.05000\ \text{L}} = 0.1000\ \text{M}$$

Because CH_3COO^- is a base, we have to use K_b and write the chemical equation for the reaction of a base with water.

$$CH_3COO^-(aq) + H_2O \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$$

$$K_b = \frac{[OH^-][CH_3COOH]}{[CH_3COO^-]} = \frac{K_w}{K_a} = 5.6 \times 10^{-10}$$

Substituting into the mass action expression gives

$$\frac{[OH^-][CH_3COOH]}{[CH_3COO^-]} = \frac{(x)(x)}{0.1000-(x)} \approx \frac{(x)(x)}{0.1000} = 5.6 \times 10^{-10}$$

$$x^2 = 3.6 \times 10^{-11} \Rightarrow x = [OH^-] = 7.5 \times 10^{-6}$$

$$[OH^-] = \sqrt{K_b \frac{M_A V_A}{V_A + V_B}}$$

The pOH calculates to be 5.12. Finally, the pH is (14.00 – 5.12) or 8.88. The pH at the equivalence point in this titration is 8.88, somewhat basic because the solution contains the Brönsted base, CH_3COO^-. *In the titration of any weak acid with a strong base, the pH at the equivalence point will be greater than 7.*

After the equivalence point, the additional OH^- now shifts the following equilibrium to the left:

$$CH_3COO^-(aq) + H_2O \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$$

The production of OH^- *by this route* is thus suppressed as we add more and more NaOH solution. The only source of OH^- that affects the pH is from the base added after the equivalence point. From here on, therefore, the pH calculations become identical to those for the last half of the titration curve for HCl and NaOH shown above. Each point is just a matter of calculating the additional number of moles of NaOH, calculating the new final volume, taking their ratio (to obtain the molar concentration), and then calculating pOH and pH (Fig. 10.7).

$$[OH^-] = \frac{M_B V_B - M_A V_A}{V_A + V_B}$$

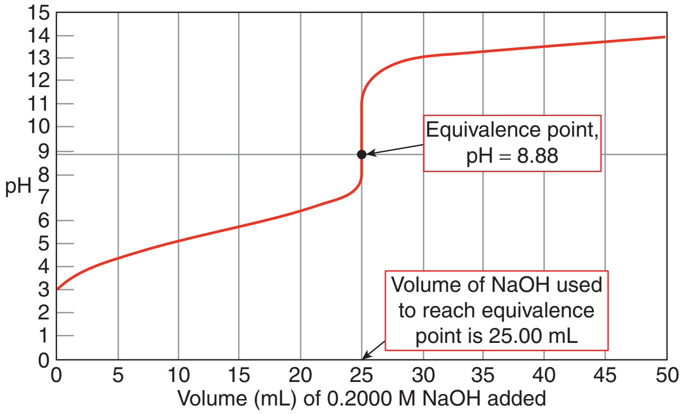


Figure 10.7 Titration curve for titrating a weak acid with a strong base.

In this titration, we follow the pH as 25.00 mL of 0.2000 M acetic acid is titrated with 0.2000 M NaOH.

Weak Base vs. Strong Acid

The calculations involved here are nearly identical to those of the weak acid–strong base titration. We will review what is required but will not actually perform the calculations.

If we titrate 25.00 mL of 0.2000 M NH_3 with 0.2000 M HCl, the molecular and net ionic equations are

$$NH_3(aq) + HCl(aq) \rightarrow NH_4Cl(aq)$$
$$NH_3(aq) + H^+(aq) \rightarrow NH_4^+(aq)$$

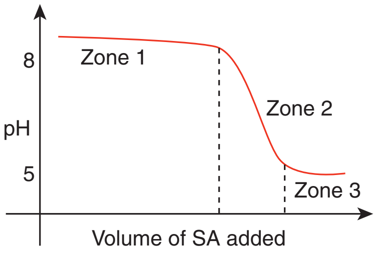


Figure 10.8 Titration curve for a weak base vs. strong acid.

Before the titration begins, the solution is simply a solution of the weak base, NH_3. Since the only solute is a base, we must use K_b to calculate the pH.

Figure 10.8 shows the plot for titration of a weak base (WB) with a strong acid (SA). From the figure:

In Zone 1: WB > SA ⇒ WBSA + WB (Basic buffer)

Thue, the curve will be flatter in this zone, as it will resist change in pH (it is a buffer solution).

In Zone 2: WB = SA ⇒WBSA

In Zone 3: WB < SA ⇒ WBSA + SA

During the titration but before the equivalence point, as we add HCl to the NH_3, the neutralization reaction produces NH_4^+, so the solution contains both NH_3 and NH_4^+ (it is a buffer solution). We do a limiting reactant calculation to determine the moles of ammonia left and the moles of ammonium ions produced by the addition of HCl. We use the equilibrium law to perform the calculation as we did with the weak acid.

At the equivalence point, all the NH_3 has reacted and the solution contains the salt NH_4Cl. We calculate the concentration of ammonium ions and then use the techniques we developed to determine the pH of the conjugate acid of a weak base.

After the equivalence point, the H^+ introduced by further addition of HCl has nothing with which to react, so it causes the solution to become more and more acidic. The concentration of H^+ calculated from the excess of HCl is used to calculate the pH. Figure 10.9 illustrates the titration curve for this system.

Titration Curves for Diprotic Acids

When a weak diprotic acid such as ascorbic acid (vitamin C) is titrated with a strong base, there are two protons to be neutralized and there are two equivalence points. Provided that the values of K_{a1} and K_{a2} differ by several powers of 10, the neutralization takes place stepwise and the resulting titration curve shows two sharp increases in pH. We would not perform the calculations here, because they are complex, but instead just look at the general shape of the titration curve, which is shown in Fig. 10.10 As each equivalence point is reached, there is a sharp rise in the pH.

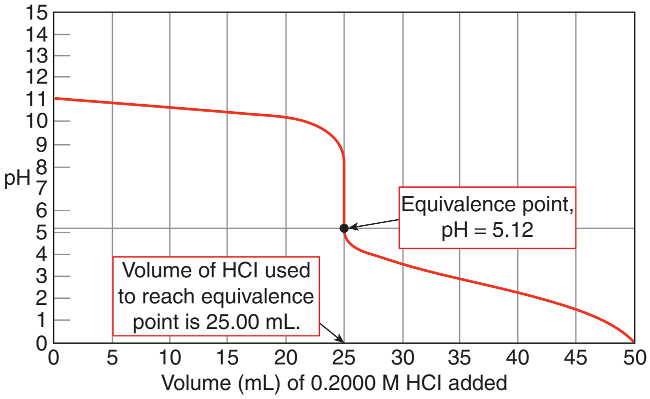


Figure 10.9 Titration curve for the titration of a weak base with a strong acid. Here we follow the pH as 25.00 mL of 0.2000 M NH_3 is titrated with 0.2000 M HCl.

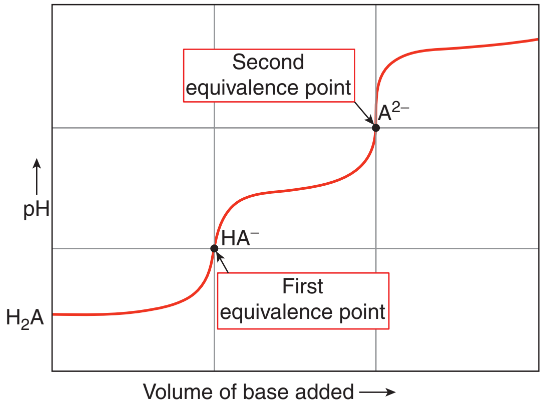


Figure 10.10 Titration of a diprotic acid, H_2A, by a strong base.

10.15 | THEORY OF INDICATORS

Indicators change color over a narrow range of pH values, as shown in Table 10.5.

Table 10.5 Common acid–base indicators

Indicator	Approximate pH range over which the color changes	Color change (Lower to higher pH)
Methyl green	0.2–1.8	Yellow to blue
Thymol blue	1.2–2.8	Yellow to blue
Methyl orange	3.2–4.4	Red to yellow
Ethyl red	4.0–5.8	Colorless to red
Methyl purple	4.8–5.4	Purple to green
Bromocresol purple	5.2–6.8	Yellow to purple
Bromothymol blue	6.0–7.6	Yellow to blue
Phenol red	6.4–8.2	Yellow to red/violet
Litmus	4.7–8.3	Red to blue
Cresol red	7.0–8.8	Yellow to red
Thymol blue	8.0–9.6	Yellow to blue
Phenolphthalein	8.2–10.0	Colorless to pink
Thymolphthalein	9.4–10.6	Colorless to blue
Alizarin yellow R	10.1–12.0	Yellow to red
Clayton yellow	12.2–13.2	Yellow to amber

Working of Indicators

Most dyes that work as acid–base indicators are also weak acids. Therefore, let's represent an indicator by the formula HIn. In its un-ionized state, HIn has one color. Its conjugate base, In^-, has a different color, the more strikingly different the better. In solution, the indicator is involved in a typical acid–base equilibrium:

$$\underset{\substack{\text{Acid form}\\\text{(one color)}}}{HIn(aq)} \rightleftharpoons H^+(aq) + \underset{\substack{\text{Base form}\\\text{(another color)}}}{In^-(aq)}$$

The corresponding acid ionization constant, K_{In}, is given by

$$K_{In} = \frac{[H^+][In^-]}{[HIn]}$$

In a strongly acidic solution, when the H^+ concentration is high, the equilibrium is shifted to the left and most of the indicator exists in its "acid form". Under these conditions, the color we observe is that of HIn. If the solution is made basic, the H^+ concentration drops and the equilibrium shifts to the right, towards In^-, and the color we observe is that of the "base form" of the indicator.

The *observed* change in color for an indicator actually occurs gradually over a range of pH values. This is because of the human eye's limited ability to discern color changes. Sometimes a change of as much as 2 pH units is needed for some indicators—more for litmus—before the eye notices the color change. This is why tables of acid–base indicators, such as Table 10.6 provide approximate pH ranges for the color changes.

In a typical acid–base titration, you have seen that as we pass the equivalence point, there is a sudden and large change in the pH. For example, in the titration of HCl with NaOH described earlier, the pH just one-half drop before the equivalence point (when 24.97 mL of the base has been added) is 3.92. Just one drop later (when 25.03 mL of base has been added) we have passed the equivalence point and the pH has risen to 10.08. This large swing in pH (from 3.92 to 10.08) causes a sudden shift in the position of equilibrium for the indicator, and we go from a condition where most of the indicator is in its acid form to a condition in which most is in the base form. This is observed visually as a change in color from that of the acid form to that of the base form.

Solved Example 10-40

An indicator is a weak acid and pH range of its color is 3.1 to 4.5. If the neutral point of the indicator lies in the center of the hydrogen ion concentrations corresponding to the given pH range, what is the ionization constant of the indicator?

Solution

We know that

$\text{pH} = -\log[\text{H}^+] \Rightarrow \log[\text{H}^+] = -\text{pH} \Rightarrow [\text{H}^+] = \text{antilog}(-\text{pH})$

For pH = 3.1,

$$[\text{H}^+]_1 = \text{antilog }(-3.1) = \text{antilog }(\bar{4}.9) = 7.94\times10^{-4}$$

For pH = 4.5,

$$[\text{H}^+]_2 = \text{antilog }(-4.5) = \text{antilog }(\bar{5}.5) = 3.16\times10^{-5}$$

Since neutral point lies at the center of the hydrogen ion concentration in the given pH range, hence $[\text{H}^+]$ at the neutral point is

$$[\text{H}^+]_2 = \frac{[\text{H}^+]_1 + [\text{H}^+]_2}{2}$$
$$= \frac{7.94\times10^{-4} + 3.16\times10^{-5}}{2} = 4.13\times10^{-4}\,\text{M}$$

Let the indicator be [HIn] that behaves as a weak acid, then $\text{HIn} + \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{ln}$

The ionization constant of the indicator K_{In} is

$$K_{\text{In}} = \frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]}$$

But at neutral point $[\text{In}^-] = [\text{HIn}]$, so $K_{\text{ln}} = [\text{H}^+] = 4.13\times 10^{-4}$ M.

Solved Example 10-41

A solution contains Na_2CO_3 and NaHCO_3. 10 mL of solution requires 2.5 mL of 0.1 M H_2SO_4 for neutralization using phenolphthalein as an indicator. Methyl orange is then added when further 2.5 mL of 0.2 M H_2SO_4 was required. Calculate the amount of Na_2CO_3 and NaHCO_3 in one liter of the solution.

Solution

The use of phenophthalien indicates half-neutralization. The reaction involved is

$$\text{Na}_2\text{CO}_3 + \text{H}^+ \rightarrow \text{NaHCO}_3 + \text{Na}^+$$

In case of methyl orange there is complete neutralization, so the reaction is

$$\text{NaHCO}_3 + \text{H}^+ \rightarrow \text{Na}^+ + \text{CO}_2 + \text{H}_2\text{O}$$

Volume of 0.1 M H_2SO_4 for complete neutralization = $2\times2.5 = 5.0$ mL.

Now, since H_2SO_4 is a dibasic acid, 0.1 M of H_2SO_4 = 0.2 N H_2SO_4 and equivalent weight of H_2SO_4 = 49.

We know that $N_1V_1\ (\text{Na}_2\text{CO}_3) = N_2V_2\ (\text{H}_2\text{SO}_4)$

Substituting values, we get

$$N_1\times10 = 0.2\times5 \Rightarrow N_1 = \frac{0.2\times5}{10} = 0.1\text{ N}$$

Equivalent weight of Na_2CO_3 = 106/2 = 53, therefore, strength of $\text{Na}_2\text{CO}_3 = 53 \times 0.1 = 5.3\text{ g L}^{-1}$

Now, for neutralization with methyl orange 0.2 M H_2SO_4 is used = 2.5 mL of 0.4 N H_2SO_4

From $N_1V_1 = N_2V_2$, we have $0.2\text{ N} \times V = 2.5 \times 0.4\text{ N} \Rightarrow V = 5$ mL

Now, from this 5 mL of H_2SO_4, 2.5 mL was used for half neutralization of Na_2CO_3, so the volume left to neutralize NaHCO_3 formed after half neutralization of Na_2CO_3 is $5.0 - 2.5 = 2.5$ mL.

Now, using $N_1V_1\ (\text{NaHCO}_3) = N_2V_2\ (\text{H}_2\text{SO}_4)$, we have

$$N_1\times10 = 0.2\times2.5 \Rightarrow N_1 = \frac{0.2\times2.5}{10} = 0.05\text{ N}$$

Equivalent weight of NaHCO_3 = 84, so strength = $84 \times 0.05 = 4.2\text{ g L}^{-1}$.

Ostwald and Quinoid Selection of Indicators

Two theories were proposed for selection of indicators. These are discussed as follows:

1. **Ostwald theory:** According to this theory, the acid–base indicator shows different color in ionized and unionized forms. The indicator is either a weak acid or a weak base. If it is a weak acid, then its ionization is faster in presence of alkalis and slower in presence of acids sue to common ion H^+. If it is a weak base then its ionization is faster in acids and slower in alkalis due to common ion OH^-. The color change in an indicator appears when it is about 50% dissociated. This theory can be illustrated with the help of following two commonly used indicators in acid–base titrations:

(a) Phenophthalein: It is an acid and can be represented as HPh. Its ionization can be represented as

$$\underset{\text{(Colorless)}}{\text{HPh}} \rightleftharpoons \text{H}^+ + \underset{\text{(Pink)}}{\text{Ph}^-}$$

From law of mass action, we have

$$K_C = \frac{[\text{H}^+][\text{Ph}^-]}{[\text{HPh}]}$$

In the presence of acid, the dissociation is almost negligible due to common ion H^+. So, the equilibrium shifts towards left and no color change is observed. However, when alkali is added, the OH^- ions remove the excess H^+ ions and shift the equilibrium to the right, thereby increasing the concentration of pink Ph^- ions. The Henderson equation can be derived for the indicator as follows. First, we represent the reaction as shown below to indicate the conjugate acid–base pairs:

$$\underset{\text{Acid}}{\text{HPh}} + \underset{\text{Base}}{\text{H}_2\text{O}} \rightleftharpoons \underset{\substack{\text{Conjugate}\\\text{acid}}}{\text{H}^+} + \underset{\substack{\text{Conjugate}\\\text{base}}}{\text{Ph}^-}$$

The ionization constant of indicator is

$$K_{\text{In}} = \frac{[\text{Ph}^-][\text{H}^+]}{[\text{HPh}]}$$

or

$$[\text{H}^+] = K_{\text{In}} \times \frac{[\text{HPh}]}{[\text{Ph}^-]}$$

$$\text{pH} = -\log_{10}[\text{H}^+] = -\log_{10}[K_{\text{In}}] - \log_{10}\frac{[\text{HPh}]}{[\text{Ph}^-]}$$

$$\text{pH} = \text{p}K_{\text{In}} + \log_{10}\frac{[\text{Ph}^-]}{[\text{HPh}]}$$

This is the Henderson equation for phenophthalien. Now, at the equivalence point, we have $[Ph^-] = [HPh]$ and $pH = pK_{In}$.

(b) Methyl orange: It is a very weak base. It is ionized to give Me^+ and OH^- ions. The reaction is as follows:

$$\underset{\text{Yellow}}{\text{MeOH}} \rightleftharpoons \underset{\text{Red}}{\text{Me}^+} + \text{OH}^-$$

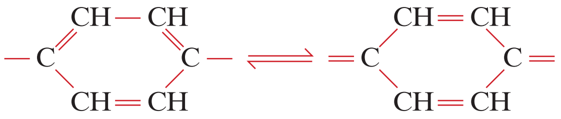
The ionization constant is

$$K = \frac{[\text{Me}^+][\text{OH}]}{[\text{MeOH}]}$$

Thus, in the presence of acid, the OH^- ions are removed and the equilibrium shifts to the right, thereby increasing the concentration of Me^+ and imparting red color to the solution. By adding alkali, the concentration of OH^- ions increases, and the equilibrium shifts to the left, thus ionization of MeOH reduces, and when it stops altogether, yellow color appears.

Note: Phenophthalein is not a good indicator for titrating weak base against strong acid, as the OH^- released by the weak base into the solution are not enough to shift the equilibrium to the right, thus the solution is not basic enough for pink color to appear. Similarly, methyl orange is not a good indicator in titration of weak acid against strong base.

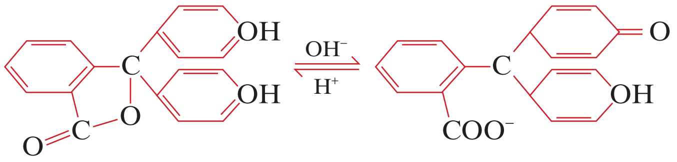
2. **Quinonoid theory:** According to this theory, acid-base indicators are aromatic organic compounds that can exist as tautomers in equilibrium with each other. One of the tautomers is in quinonoid form while the other is in benzenoid form.


Benzenoid form Quinonoid form

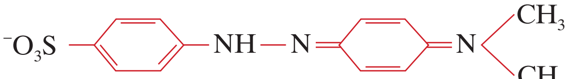
One of the forms is generally more stable in acidic medium and the other in basic medium, so inter-conversion between the two forms takes place with change in pH. This change is reflected as change in color of the solution because the quinonoid form generally has deeper color than the benzenoid form.

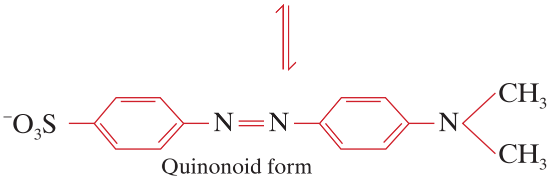
Let us again consider the examples of phenolphthalein and methyl orange.

(a) **Phenolphathalein:** It exists in benzenoid form in acidic medium and is colorless and changes to quinonoid form in alkaline medium which has pink color.


Benzenoid form (stable in acid, colorless) Quinonoid form (stable in alkali, pink in color)

(b) **Methyl orange:** It exists in benzenoid form in alkaline medium and is colorless or yellow in color. In acidic medium, the quinonoid form with red color is more stable.


Benzenoid form
(stable in alkali, coloriess or yellow)


Quinonoid form
(stable in acid, red in color)

10.16 | SOLUBILITY EQUILIBRIA OF SPARINGLY SOLUBLE SALTS

Solubility is defined as the concentration of a saturated solution of a solute in a given solvent at a particular temperature. It depends on the nature of the solute and solvent, and the temperature and pressure conditions. Different ionic solids (salts) show different solubility in water. Some salts are very soluble and can even absorb moisture from the air. These are said to be hygroscopic and are generally used for drying solids or for removal of moisture from solvents. Calcium chloride is an example. Some salts, such as lithium fluoride have little solubility in water and are practically considered insoluble. The solubility of an ionic solute in water or any other solvent is determined by two competing energy considerations:

1. Lattice enthalpy, which holds the oppositely charged ions together in the salt.
2. Solvation enthalpy, which is the energy released on solvation of ions in solution.

For a salt to dissolve in solution, the strong forces of attraction between ions must be overcome by the energy released on their solvation. The solvation energy is determined by the nature and polarity of the solvent. Polar solvents have high energy of solvation and are hence able to overcome the lattice enthalpy of the ions in the solid. Non-polar (covalent) solvents have low solvation enthalpy that does not compete favorably with the lattice enthalpy, hence ionic solid are insoluble in non-polar solvents. Based on solubility of salts, they can be classified as:

Soluble	Solubility > 0.1 M
Slightly soluble	0.01 M< Solubility < 0.1 M
Sparingly soluble	Solubility < 0.01 M

A large number of ionic solids fall into the category of being sparingly soluble in water. A small amount dissolves in water and once the solution is saturated, an equilibrium is established between undissolved salts and its ions in the solution.

Solubility Product Constant

When AgCl is placed in water, a very small amount of it dissolves in water and we say that the salt is sparingly soluble in water. Once the solution has become saturated, the following equilibrium is established between the undissolved AgCl and its ions in solution.

$$\mathrm{AgCl(s)} \rightleftharpoons \mathrm{Ag^+(aq)} + \mathrm{Cl^-(aq)}$$

This is a heterogeneous equilibrium because it involves a solid reactant (AgCl) in equilibrium with ions in aqueous solution. At equilibrium, the solute continues to dissolve at a rate that exactly matches the backward process. Such a solution is a saturated solution, wherein the dissolved and undissolved solutes are in equilibrium with each other. The solubility of a substance in a solvent is the concentration in the solution.

We can write the equilibrium law as follows. Applying law of mass action to the above reaction, we get

$$K = \frac{[\mathrm{Ag^+}][\mathrm{Cl^-}]}{[\mathrm{AgCl}]}$$

As the amount of AgCl in contact with saturated solution does not change with time, so the factor [AgCl] remains constant. Thus,

$$K_{\mathrm{sp}} = [\mathrm{Ag^+}][\mathrm{Cl^-}] \tag{10.31}$$

The equilibrium constant, K_{sp}, is called the **solubility product constant** (because the system is a *solubility* equilibrium and the constant equals a *product* of ion concentrations). It equals the ionic product of a saturated electrolyte solution. Ionic product is the reaction quotient (Q) for the equilibrium. At equilibrium, ionic product = solubility product.

It is important to understand the distinction between solubility and solubility product. The *solubility* of a salt is the amount of the salt that dissolves in a given amount of solvent to give a saturated solution. The *solubility product* is the product of the molar concentrations of the ions in the saturated solution, raised to appropriate powers.

In general, consider the dissociation of any sparingly soluble electrolyte, $\mathrm{A}_x\mathrm{B}_y$

$$\mathrm{A}_x\mathrm{B}_y \rightleftharpoons x\mathrm{A}^{y+} + y\mathrm{B}^{x-}$$

Applying the law of mass action, we get

$$K = \frac{[\mathrm{A}^{y+}]^x[\mathrm{B}^{x-}]^y}{[\mathrm{A}_x\mathrm{B}_y]}$$

In saturated solution, $[\mathrm{A}_x\mathrm{B}_y] = \text{constant} = K'$

Thus, $[\mathrm{A}^{y+}]^x[\mathrm{B}^{x-}]^y = K[\mathrm{A}_x\mathrm{B}_y] = KK' = K_{\mathrm{sp}}$

where $[\mathrm{A}^{y+}]$ and $[\mathrm{B}^{x-}]$ are the ionic concentrations in a saturated solution. Thus, the solubility product of an electrolyte may be defined as

The maximum product of the concentrations of the constituent ions each raised to the power equal to its ions present in the equation representing the solution of one molecule of the electrolyte.

For a saturated solution, the ionic product is equal to the solubility product. However, for an unsaturated solution, the ionic product is less than the solubility product; and for a supersaturated solution it is more than the solubility product.

Solubility of a solute is expressed as moles of solid solute dissolved per liter of solution and is represented as S. For example, for the reaction

$$\mathrm{AgCl(s)} \rightleftharpoons \mathrm{Ag^+(aq)} + \mathrm{Cl^-(aq)}$$

If S is the solubility of AgCl, then the equilibrium concentrations of Ag^+ and Cl^- are $[Ag^+] = S$ mol L^{-1} and $[Cl^-] = S$ mol L^{-1}. Substituting the values in the expression for solubility product, we get

$$K_{sp} = [\mathrm{Ag^+}][\mathrm{Cl^-}] = [S\ \mathrm{mol\ L^{-1}}][S\ \mathrm{mol\ L^{-1}}] = S^2\ \mathrm{mol^2 L^{-2}}$$

In general, consider the general form of electrolyte A_xB_y which dissociates as

$$\mathrm{A}_x\mathrm{B}_y = x[\mathrm{A}^{y+}] + y[\mathrm{B}^{x-}]$$

Therefore,

$$K_{sp} = [\mathrm{A}^{y+}]^x[\mathrm{B}^{x-}]^y$$

Let S mol L^{-1} be the solubility of the electrolyte, then concentration of the ions is

$$[\mathrm{A}^{y+}] = xS\ \mathrm{mol\ L^{-1}}\ \text{and}\ [\mathrm{B}^{x-}] = yS\ \mathrm{mol\ L^{-1}}$$

Substituting the values of $[A^{y+}]$ and $[B^{x-}]$ in the above equation, we get

$$K_{sp} = [xS]^x[yS]^y = x^x \times y^y \times S^{x+y}$$

Therefore, solubility can be given by

$$S^{x+y} = \frac{K_{sp}}{x^x \times y^y} \Rightarrow S = \left(\frac{K_{sp}}{x^x \times y^y}\right)^{1/x+y} \tag{10.32}$$

When the concentrations of one or more terms does not correspond to the equilibrium concentration, the term K_{sp} can be replaced by Q_{sp}.

The solubilities of salts change with temperature, so a value of K_{sp} applies only at the temperature at which it was determined. Some typical K_{sp} values are given in Table 10.6.

Table 10.6 Typical K_{sp} values for some salts

Type	Salt		Ions of salt	K_{sp} (25°C)	Type	Salt		Ions of salt	K_{sp} (25°C)
Halides	CaF_2	$\rightleftharpoons$	$Ca^{2+} + 2F^-$	3.9×10^{-11}	**Carbonates**	$SrCO_3$	$\rightleftharpoons$	$Sr^{2+} + CO_3^{2-}$	9.3×10^{-10}
	AgCl	$\rightleftharpoons$	$Ag^+ + Cl^-$	1.8×10^{-10}		$BaCO_3$	$\rightleftharpoons$	$Ba^{2+} + CO_3^{2-}$	5.0×10^{-9}
	AgBr	$\rightleftharpoons$	$Ag^+ + Br^-$	5.0×10^{-13}		$CoCO_3$	$\rightleftharpoons$	$Co^{2+} + CO_3^{2-}$	1.0×10^{-10}
	AgI	$\rightleftharpoons$	$Ag^+ + I^-$	8.3×10^{-17}		$NiCO_3$	$\rightleftharpoons$	$Ni^{2+} + CO_3^{2-}$	1.3×10^{-7}

(*Continued*)

Table 10.6 (Continued)

Type	Salt		Ions of salt	K_{sp} (25°C)	Type	Salt		Ions of salt	K_{sp} (25°C)
	PbF_2	$\rightleftharpoons$	$Pb^{2+} + 2F^-$	3.6×10^{-8}		$ZnCO_3$	$\rightleftharpoons$	$Zn^{2+} + CO_3^{2-}$	1.0×10^{-10}
	$PbCl_2$	$\rightleftharpoons$	$Pb^{2+} + 2Cl^-$	1.7×10^{-5}	**Chromates**	Ag_2CrO_4	$\rightleftharpoons$	$2Ag^+ + CO_3^{2-}$	1.2×10^{-12}
	$PbBr_2$	$\rightleftharpoons$	$Pb^{2+} + 2Br^-$	2.1×10^{-6}		$PbCrO_4$	$\rightleftharpoons$	$Pb^{2+} + CO_3^{2-}$	1.8×10^{-14}
	PbI_2	$\rightleftharpoons$	$Pb^{2+} + 2I^-$	7.9×10^{-9}	**Sulphates**	$CaSO_4$	$\rightleftharpoons$	$Ca^{2+} + SO_4^{2-}$	2.4×10^{-5}
Hydroxides	$Al(OH)_3$	$\rightleftharpoons$	$Al^{3+} + 3OH^-$	3×10^{-34}		$SrSO_4$	$\rightleftharpoons$	$Sr^{2+} + SO_4^{2-}$	3.2×10^{-7}
	$Ca(OH)_2$	$\rightleftharpoons$	$Ca^{2+} + 2OH^-$	6.5×10^{-6}		$BaSO_4$	$\rightleftharpoons$	$Ba^{2+} + SO_4^{2-}$	1.1×10^{-10}
	$Fe(OH)_2$	$\rightleftharpoons$	$Fe^{2+} + 2OH^-$	7.9×10^{-16}		$PbSO_4$	$\rightleftharpoons$	$Pb^{2+} + SO_4^{2-}$	6.3×10^{-7}
	$Fe(OH)_3$	$\rightleftharpoons$	$Fe^{3+} + 3OH^-$	1.6×10^{-39}	**Oxalates**	CaC_2O_4	$\rightleftharpoons$	$Ca^{2+} + C_2O_4^{2-}$	2.3×10^{-9}
	$Mg(OH)_2$	$\rightleftharpoons$	$Mg^{2+} + 2OH^-$	7.1×10^{-12}		MgC_2O_4	$\rightleftharpoons$	$Mg^{2+} + C_2O_4^{2-}$	8.6×10^{-5}
	$Zn(OH)_2$	$\rightleftharpoons$	$Zn^{2+} + 2OH^-$	3.0×10^{-16}		BaC_2O_4	$\rightleftharpoons$	$Ba^{2+} + C_2O_4^{2-}$	1.2×10^{-7}
Carbonates	Ag_2CO_3	$\rightleftharpoons$	$2Ag^+ + CO_3^{2-}$	8.1×10^{-12}		FeC_2O_4	$\rightleftharpoons$	$Fe^{2+} + C_2O_4^{2-}$	2.1×10^{-7}
	$MgCO_3$	$\rightleftharpoons$	$Mg^{2+} + CO_3^{2-}$	3.5×10^{-8}		PbC_2O_4	$\rightleftharpoons$	$Pb^{2+} + C_2O_4^{2-}$	2.7×10^{-11}
	$CaCO_3$	$\rightleftharpoons$	$Ca^{2+} + CO_3^{2-}$	4.5×10^{-9}					

Relation with Ionic Product

For a salt solution at a specified concentration, the product of the concentration of the ions, each raised to the appropriate power, is called as the ionic product for a saturated solution in equilibrium with excess of solid.

1. If ionic product = solubility product, the solution is in equilibrium.
2. If ionic product < solubility product, the solution is unsaturated and more salt can be dissolved in it.
3. If ionic product > solubility product, then the solution is containing more salt than it can dissolve, therefore, precipitation starts and continues till ionic product becomes equal to solubility product.

Calculation of Solubility of Salts

1. **K_{sp} can be determined from molar solubilities:** Molar solubility equals the number of moles of the salt dissolved in one liter of its saturated solution. The molar solubility can be used to calculate the K_{sp} under the assumption that all of the salt that dissolves is 100% dissociated into ions implied by the salt's formula.
2. **Molar solubility can be calculated from K_{sp}:** The equilibrium concentrations can be calculated algebraically by defining an unknown x as the molar solubility of the salt and making substitutions in expression for K_{sp}.

The solubilities of some salts under various conditions are calculated as follows.

1. Consider solubility of AgCl various solutions.
   (a) Solubility in water: The reaction at saturation point is

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

If the solubility of the salt is S mol L^{-1}, then $[Ag^+] = S$ M and $[Cl^-] = S$ M

So, $$K_{sp} = S^2 \Rightarrow S = \sqrt{K_{sp}} = \sqrt{10^{-5}} = 0.00316 \text{ mol L}^{-1}.$$

   (b) Solubility in a solution that is having 0.1 M in $AgNO_3$: The reaction at saturation point is

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

The K_{sp} of AgCl ≅ 10^{-10}. If AgCl dissolved in pure water, its solubility would have been 10^{-5} M. However, in the presence of 0.1 M $AgNO_3$, the solubility of AgCl decreases due to common ion effect. Therefore, $[Ag^+]$ from AgCl would be less than 10^{-5} M and can be ignored.

Let the solubility of AgCl be S_1 mol L^{-1} in the presence of 0.1 M $AgNO_3$, then $[Ag^+] = 0.1$ M and $[Cl^-] = S_1$ M, or

$$S_1 = \frac{K_{sp}}{0.1} = 10^{-9}\,\text{mol L}^{-1}$$

2. Consider solubility of CH_3COOAg in various solutions.

(a) Solubility in water: Since CH_3COOAg is a salt of weak acid and strong base, it would hydrolyze in water. If the solubility of the salt is x mol L^{-1} then we have

$$CH_3COOAg(s) \rightleftharpoons \underset{x-y}{CH_3COO^-(aq)} + \underset{x}{Ag^+(aq)}$$

At equilibrium, the reaction is $\underset{x-y}{CH_3COO^-(aq)} + H_2O \rightleftharpoons \underset{y}{CH_3COOH(aq)} + \underset{x}{H^+(aq)}$

where y is the amount of CH_3COO^- ion that is hydrolyzed. The solubility product is

$$K_{sp} = (x-y)x$$

and

$$\frac{y^2}{(x-y)} = \frac{K_w}{K_a}$$

Knowing the values of K_{sp} and K_a, solubility of the salt can be calculated.

(b) Solubility in an acid buffer of pH = 4 (assuming that the buffer does not have any common ion by CH_3COOAg): It was found that CH_3COOAg dissolves, reaches equilibrium, and then gets hydrolyzed. If the solubility of the salt is x_1 M in this solution, then we have

$$CH_3COOAg(s) \rightleftharpoons \underset{x_1-y_1}{CH_3COO^-(aq)} + \underset{x_1}{Ag^+(aq)}$$

At equilibrium, the reaction is $\underset{x_1-y_1}{CH_3COO^-(aq)} + H_2O \rightleftharpoons \underset{y_1}{CH_3COOH(aq)} + \underset{10^{-10}}{OH^-(aq)}$

where y_1 the extent to which it is hydrolyzed. Since the solution is a buffer, the pH will be maintained. The solubility product is

$$K_{sp} = (x_1 - y_1)x_1$$

and

$$\frac{y_1 \times 10^{-10}}{(x_1 - y_1)} = \frac{K_w}{K_a}$$

Knowing K_{sp} and K_a, the solubility can be calculated.

(c) Solubility of CH_3COOAg in an buffer solution of pH = 9: Following the same steps as in the points above, and considering solubility of the salt is x_2 M in this solution we get

$$CH_3COOAg(s) \rightleftharpoons \underset{x_2-y_2}{CH_3COO^-(aq)} + \underset{x_2}{Ag^+(aq)}$$

At equilibrium, the reaction is $\underset{x_2-y_2}{CH_3COO^-(aq)} + H_2O \rightleftharpoons \underset{y_2}{CH_3COOH(aq)} + \underset{10^{-4}}{OH^-(aq)}$

where y_2 the extent to which it is hydrolyzed. Since the solution is a buffer, the pH will be maintained. The solubility product is

$$K_{sp} = (x_2 - y_2)x_2$$

and
$$\frac{y_2 \times 10^{-5}}{(x_2 - y_2)} = \frac{K_w}{K_a}$$

Knowing K_{sp} and K_a, the solubility can be calculated.

3. **Simultaneous solubility:** Consider the following example

$$\underset{S_1}{\text{AgCl}} \rightleftharpoons \underset{S_1+S_2}{\text{Ag}^+} + \underset{S_1}{\text{Cl}^-} \qquad (K_{\text{sp(AgCl)}})$$
$$\underset{S_2}{\text{AgBr}} \rightleftharpoons \underset{S_2+S_1}{\text{Ag}^+} + \underset{S_2}{\text{Br}^-} \qquad (K_{\text{sp(AgBr)}})$$

Therefore,

$$K_{\text{sp(AgCl)}} = (S_1 + S_2)(S_1)$$
$$K_{\text{sp(AgBr)}} = (S_1 + S_2)(S_2)$$

Therefore,

$$S_1 + S_2 = \sqrt{K_{\text{sp(AgCl)}} + K_{\text{sp(AgBr)}}}$$
$$S_1 = \frac{K_{\text{sp(AgCl)}}}{\sqrt{K_{\text{sp(AgCl)}} + K_{\text{sp(AgBr)}}}}$$
$$S_2 = \frac{K_{\text{sp(AgBr)}}}{\sqrt{K_{\text{sp(AgCl)}} + K_{\text{sp(AgBr)}}}}$$

4. **Complexation equilibrium:** Solubility in an aqueous solution containing NH_3: Let the amount of NH_3 initially be a M. If the solubility of the salt is x mol L^{-1}, then we have

$$\text{AgCl(s)} \rightleftharpoons \underset{x-y}{\text{Ag}^+\text{(aq)}} + \underset{x}{\text{Cl}^-\text{(aq)}}$$

At equilibrium, the reaction is

$$\underset{x-y}{\text{Ag}^+\text{(aq)}} + \underset{a-2y}{2\text{NH}_3\text{(aq)}} \rightleftharpoons \underset{y}{[\text{Ag(NH}_3)_2]^+\text{(aq)}}$$

where y is the amount of Ag^+ which has reacted with NH_3. The solubility product is

$$K_{sp} = (x - y)x$$

and
$$\frac{y}{(x-y)(a-2y)^2} = K_f$$

where K_f is the formation constant $[Ag(NH_3)_2]^+$. Knowing the values of K_{sp} and K_f, solubility of the salt can be calculated.

Solved Example 10-42

If 10^{-3} mol of Cu^{2+}, Co^{2+} and Ag^+ are provided, calculate the amount of NH_3 required to be added to 1 L of the solution of each in order to lower the uncomplexed metal ion to 10^{-4} M.

Given:

$$[\text{Cu(NH}_3)_4]^{2+} \rightleftharpoons \text{Cu}^{2+} + 4\text{NH}_3 \qquad k_{\text{inst},1} = 10^{-12}$$
$$[\text{Co(NH}_3)_6]^{2+} \rightleftharpoons \text{Co}^{2+} + 6\text{NH}_3 \qquad k_{\text{inst},2} = 4 \times 10^{-5}$$
$$[\text{Ag(NH}_3)_2]^{+} \rightleftharpoons \text{Ag}^{+} + 2\text{NH}_3 \qquad k_{\text{inst},3} = 6 \times 10^{-8}$$

Solution

After the addition of ammonia, final concentration of each ion should be $[Cu^{2+}] = [Co^{2+}] = [Ag^+] = 10^{-4}$ M

Therefore,

$$[Cu(NH_3)_4]^{2+} = [Co(NH_3)_6]^{2+} = [Ag(NH_3)_2]^{+}$$
$$= 10^{-3} - 10^{-4}$$

Since, all the complexes are formed completely from the ions reacted

$$k_{inst,1} = 10^{-12} = \frac{[NH_3]^4[Cu^{2+}]}{[Cu(NH_3)_4]^{2+}}$$

$$10^{-12} = \frac{[NH_3]^4(10^{-4})}{(9\times 10^{-4})}$$

Therefore, $[NH_3]$ in Cu^{2+} solution = 1.73×10^{-3} M

$$k_{inst,2} = 4\times 10^{-5} = \frac{[Co^{2+}]^4[NH_3]^6}{[Co(NH_3)_6]^{2+}}$$

$$4\times 10^{-5} = \frac{(10^{-4})[NH_3]^6}{(9\times 10^{-4})}$$

Therefore, $[NH_3]$ in Co^{2+} solution = 2.67×10^{-1} M

$$k_{inst,3} = 6\times 10^{-8} = \frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2]^+}$$

$$6\times 10^{-8} = \frac{(10^{-4})[NH_3]^2}{(9\times 10^{-4})}$$

Therefore, $[NH_3]$ in Ag^+ solution = 7.35×10^{-4} M

Actual NH_3 to be added = Free NH_3 + Combined NH_3

NH_3 to be added to Cu^{2+} solution $= 1.73\times 10^{-3} + 4(9\times 10^{-4})$
$= 5.33 \times 10^{-3}$ M

NH_3 to be added to Co^{2+} solution $= 2.67\times 10^{-1} + 6(9\times 10^{-4})$
$= 2.72 \times 10^{-3}$ M

NH_3 to be added to Ag^+ solution $= 7.35\times 10^{-4} + 2(9\times 10^{-4})$
$= 2.535 \times 10^{-3}$ M

Solved Example 10-43

The solubility of thallium(I) iodide, TlI, in water at 20°C is 5.9×10^{-3} g L^{-1}. Using this fact, calculate K_{sp} for TlI on the assumption that it is 100% dissociated in the solution.

Solution

The reaction involved is $TlI(s) \rightleftharpoons Tl^+(aq) + I^-(aq)$

$$\text{Moles of TlI} = 5.9\times 10^{-3}\ \text{g}\left(\frac{1}{331.3}\right) = 1.78\times 10^{-5}\ \text{mol}$$

Concentration of $[Tl^+] = [I^-] = \dfrac{1.78\times 10^{-5}\ \text{mol}}{1L} = 1.78 \times 10^{-5}$ M

Therefore, $K_{sp} = [Tl^+]\,[I^-] = (1.8\times 10^{-5})(1.8\times 10^{-5})$
$= 3.2\times 10^{-10}$

Solved Example 10-44

What is the calculated molar solubility in water at 25°C of **(a)** AgBr and **(b)** Ag_2CO_3?

Solution

(a) The reaction is

	$AgBr(s) \rightleftharpoons$	$Ag^+(aq) +$	$Br^-(aq)$
Initial concentration	x	0	0
Equilibrium concentration	$1-x$	x	x

Substituting the above values for equilibrium concentrations into the expression for K_{sp} gives:

$$K_{sp} = 5.0\times 10^{-13} = [Ag^+][Br^-] = (x)(x)$$

or $\quad x = \sqrt{5.0\ \times\ 10^{-13}} = 7.1\times 10^{-7}$

Thus, the solubility is 7.1×10^{-7} M AgBr.

(b) The reaction is

	$Ag_2CO_3(s) \rightleftharpoons$	$2Ag^+(aq) +$	$CO_3^{2-}(aq)$
Initial concentration	x	0	0
Equilibrium concentration	$1-x$	$2x$	x

Substituting the above values for equilibrium concentrations into the expression for K_{sp} gives:

$$K_{sp} = 8.1\times 10^{-12} = [Ag^+]^2\,[CO_3^{2-}]$$
$$= (2x)^2(x) \text{ and } 4x^3 = 8.1\times 10^{-12}$$

or $\quad x = \left[\dfrac{(8.1\times 10^{-12})}{4}\right]^{1/3} = 1.3\times 10^{-4}$

Thus, the molar solubility is 1.3×10^{-4} M Ag_2CO_3.

Solved Example 10-45

Calculate the molar solubility of $Fe(OH)_3$ in a solution where the OH^- concentration is initially 0.050 M. Assume the dissociation of $Fe(OH)_3$ is 100%.

Solution

The reaction is

$$Fe(OH)_3(s) \rightleftharpoons Fe^{3+}(aq) + 3OH^-(aq)$$

Initial concentration	x	0	0
Equilibrium concentration	$1-x$	x	$0.050+3x$

Substituting the above values for equilibrium concentrations into the expression for K_{sp} gives:

$$K_{sp} = 1.6 \times 10^{-39} = [Fe^{3+}]\,[OH^-]^3 = (x)[0.050 + 3x]^3$$

We try to simplify by making the approximation that $(0.050 + 3x) \approx 0.050$:

$$1.6 \times 10^{-39} = (x)\,(0.050)^3 \Rightarrow x = 1.3 \times 10^{-35}$$

Clearly the assumption that $(0.050 + 3x) \approx 0.050$ is justified. Thus 1.3×10^{-35} M of $Fe(OH)_3$ will dissolve in a 0.050 M sodium hydroxide solution.

Solved Example 10-46

The $[Ag^+]$ ion in a saturated solution of Ag_2CrO_4 at 25°C is 1.5×10^{-4} M. What is the K_{sp} of Ag_2CrO_4 at 25°C?

Solution

For saturated solution of Ag_2CrO_4, if solubility is S mol L^{-1}. Then,

$$AgCrO_4(s) \rightleftharpoons \underset{2S}{2Ag^+(aq)} + \underset{S}{CrO_4^-(aq)}$$

$$AgCrCO_4\,(s) \rightleftharpoons 2Ag^+\,(aq) + CrO_4^{2-}\,(aq)$$

The solubility product is $K_{sp} = [Ag^+]\,[CrO_4^-] = (2S)^2\,(S)$
$= 4S^3$

Given that $[Ag^+] = 2S = 1.5 \times 10^{-4} \Rightarrow S = 0.75 \times 10^{-4}$. Substituting in the above expression, we get

$$K_{sp} = 4(0.75 \times 10^{-4})^3 = 1.688 \times 10^{-12}\ \text{mol}^3\ \text{L}^{-3}$$

Solved Example 10-47

A 100.0 mL sample is removed from an aqueous solution saturated with $CaSO_4$ at 25°C. The water is completely evaporated from the sample and a deposit of 0.24 g $CaSO_4$ is obtained. Calculate the K_{sp} for $CaSO_4$ at 25°C.

Solution

The reaction is $CaSO_4(s) \rightleftharpoons Ca^{2+}(aq) + SO_4^{2-}(aq)$. Given that the solubility of $CaSO_4$ is 0.24 g per 100 mL. Now,

$$[CaSO_4] = \frac{0.24}{100} \times \frac{1000}{136}\ \text{mol L}^{-1}$$
$$= 0.01765\ \text{M}$$

So, $$[Ca^{2+}] = [SO_4^{2-}] = 0.01765\ \text{M}$$

Substituting in K_{sp} expression, we get

$$K_{sp} = [Ca^{2+}][SO_4^{2-}] = (0.01765)^2 = 3.115 \times 10^{-4}.$$

Effect of Common Ion on Solubility

The presence of a common ion in the solution decreases the solubility of a given substance. For example, the solubility of $BaSO_4$ in Na_2SO_4 solution is smaller than that in an aqueous solution. The following two examples are discussed to bring in more clarity on the effect of common ion on solubility.

1. Consider saturated solution of AgCl. If a salt having either of the ion common to AgCl say KCl is added to it, then the reaction at equilibrium are

$$AgCl(s) \rightleftharpoons Ag^+ + C1^-$$
$$KCl(s) \rightarrow K^+ + C1^-$$

For AgCl, the solubility product is $K_{sp} = [Ag^+][C1^-]$. We see that $[Cl^-]$ increases in solution due to presence of KCl. To keep the solubility product constant, $[Ag^+]$ needs to decrease or AgCl needs to precipitate out from solution, that is, solubility of AgCl will decrease with increasing concentration of KCl in solution. If a 0.1 M solution of KCl is added to AgCl solution of solubility S mol L^{-1}, then, for AgCl

$$K_{sp} = [Ag^+][Cl^-] = S(S + 0.1)$$

as $S \ll 0.1$, it may be neglected, therefore, we have

$$K_{sp} = S \times 0.1 \Rightarrow S_{AgCl} = \frac{K_{sp}}{0.1}$$

2. Suppose that we stir some lead chloride (a compound having a low solubility) with water long enough to establish the following equilibrium.

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$$

If we now add a concentrated solution of a soluble lead compound, such as $Pb(NO_3)_2$, the increased concentration of Pb^{2+} in the $PbCl_2$ solution will drive the position of equilibrium to the left, causing some $PbCl_2$ to precipitate. The phenomenon is simply an application of Le Chatelier's principle, the net result being that $PbCl_2$ is less soluble in a solution that contains Pb^{2+} from another source than it is in pure water. The same effect is produced if a concentrated solution of a soluble chloride salt such as NaCl is added to the saturated $PbCl_2$ solution. The added Cl^- will drive the equilibrium to the left, reducing the amount of dissolved $PbCl_2$. This phenomenon can be described as an example of common ion effect, where Pb^{2+} is the common ion when we add $Pb(NO_3)_2$ and Cl^- is the common ion when we add NaCl. The common ion effect can dramatically lower the solubility of a salt, even a relatively soluble salt, NaCl, can be forced out of its saturated solution simply by adding concentrated hydrochloric acid, which serves as a source of the common ion, Cl^-.

If we know the anticipated concentrations of the ions of a salt in a solution, we can use the value of K_{sp} for the salt to predict whether or not a precipitate should form. This is because the computed value for Q (the ion product) can tell us whether a solution is unsaturated, saturated or supersaturated. *For a precipitate of a salt to form, the solution must be supersaturated*.

If the solution is unsaturated, its ion concentrations are less than required for saturation, Q is less than K_{sp}, and no precipitate should form. For a saturated solution, we have Q equal to K_{sp}, and no precipitate will form. (If a precipitate were to form, the solution would become unsaturated and the precipitate would redissolve.) If the solution is supersaturated, the ion concentrations exceed those required for saturation and Q is larger than K_{sp}. Only in this last instance should we expect a precipitate to form. This can be summarized as follows.

Precipitate will form	$Q > K_{sp}$	Supersaturated
No precipitate	$Q = K_{sp}$	Saturated
	$Q < K_{sp}$	Unsaturated

Solved Example 10-48

The solubility product of AgCl at 25°C is 1.8×10^{-10}. What is the solubility of AgCl in **(a)** pure water, **(b)** 0.1 M $AgNO_3$ and **(c)** 0.01 M NaCl?

Solution

Let solubility of AgCl be S mol L^{-1}.

(a) The reaction involved is $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$. The solubility product is given by

$$K_{sp} = [Ag^+][Cl^-] = S \times S$$

Therefore, solubility $= S = (K_{sp})^{1/2} = (1.8 \times 10^{-10})^{1/2} = 1.34 \times 10^{-5}$ mol L^{-1}.

(b) The reactions involved are

$$AgCl(s) \rightleftharpoons \underset{S}{Ag^+(aq)} + \underset{S}{Cl^-(aq)}$$

$$AgNO_3(s) \rightleftharpoons \underset{0.1}{Ag^+(aq)} + \underset{0.1}{NO_3^-(aq)}$$

Therefore, the solubility product is $K_{sp} = [Ag^+][Cl^-] = (0.1 + S)(S)$.

$S \ll 0.1$ as the presence of common ion decreases solubility. So, we have

$$S(0.1) = 1.8\times10^{-10} \Rightarrow S = 1.8\times10^{-9}\ \text{mol L}^{-1}$$

Therefore, $S = 1.5$.

(c) The reactions involved are

$$AgCl(s) \rightleftharpoons \underset{S}{Ag^+(aq)} + \underset{S}{Cl^-(aq)}$$

$$NaCl(s) \rightleftharpoons \underset{0.01}{Na^+(aq)} + \underset{0.01}{Cl^-(aq)}$$

The solubility product is $K_{sp} = [Na^+][Cl^-] = (0.01 + S)(S)$. $S \ll 0.01$ as the presence of common ion decreases solubility. So, we have

$$S(0.01) = 1.8\times10^{-10} \Rightarrow S = 1.8\times10^{-8}\ \text{mol L}^{-1}$$

Solved Example 10-49

The solubility product of SrF_2 in water is 8×10^{-10}, then what is its solubility in 0.1 M NaF aqueous solution?

Solution

We know that $K_{sp} = [Sr^{2+}][F^-]^2 \Rightarrow 8\times10^{-10} = S[2S + 0.1]^2$

Thus, $$S = \frac{8\times10^{-10}}{(0.1)^2} = 8\times10^{-8}\,\text{M}$$

Solved Example 10-50

The K_{sp} for barium oxalate, BaC_2O_4, is 1.2×10^{-7} and for oxalic acid, $H_2C_2O_4$, $K_{a1} = 5.6\times10^{-2}$ and $K_{a2} = 5.4\times10^{-5}$. If a solution containing 0.10 M $H_2C_2O_4$ and 0.050 *M* $BaCl_2$ is prepared, what must the minimum H^+ concentration be in the solution to prevent the formation of a BaC_2O_4 precipitate? (Hint: Work with a combined K_a expression for $H_2C_2O_4$.)

Solution

The reaction involved is

$$BaC_2O_4(s) \rightleftharpoons Ba^{2+}(aq) + C_2O_4^{2-}(aq)$$

with $K_{sp} = 1.2\times10^{-7} = [Ba^{2+}][C_2O_4^{2-}]$.
Given that $[Ba^{2+}] = 0.050$ M, so we have

$$1.2\times10^{-7} = (0.050)[C_2O_4^{2-}] \Rightarrow [C_2O_4^{2-}] = 2.4\times10^{-6}\ \text{M}$$

$H_2C_2O_4$ dissociates as follows:

$$H_2C_2O_4 \rightleftharpoons H^+ + HC_2O_4^- \qquad K_{a1} = 5.6\times10^{-2}$$

$$HC_2O_4^- \rightleftharpoons H^+ + C_2O_4^{2-} \qquad K_{a2} = 5.4\times10^{-5}$$

$$H_2C_2O_4 \rightleftharpoons 2H^+ + C_2O_4^{2-} \qquad K_a = (5.4\times10^{-5})\times(5.6\times10^{-2}) = 3.0\times10^{-6}$$

Now, $[H_2C_2O_4] = 0.10$ (given) and $[C_2O_4^{2-}] = 2.4\times10^{-6}$ M, so we have

$$K_a = 3.0\times10^{-6} = \frac{[H^+]^2[C_2O_4^{2-}]}{[H_2C_2O_4]} = \frac{[H^+]^2\times(2.4\times10^{-6})}{(0.10)},$$

we get $[H^+] = 3.54\times10^{-1}$ M

This is the minimum concentration of H^+ that will prevent the formation of BaC_2O_4 precipitate.

Effect of Hydrolysis on Solubility

Consider the following hydrolysis reactions for CH_3COOAg

$$CH_3COOAg \rightleftharpoons CH_3COO^- + Ag^+$$
$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

Here, $[CH_3COO^-]$ is consumed in the second reaction. Therefore, the equilibrium of first reaction should shift in the forward direction according to the Le Chaterlier's principle. Thus, the solubility should increase on hydrolysis.

Effect of pH on Solubility

It is possible to alter the solubility of some substances, particularly salts of weak acids, by controlling the pH of the solution. As the pH is lowered, the concentration of anion is lowered due to its protonation which in turn increases the solubility of the salt to bring back $K_{sp} = Q_{sp}$. We, thus, need to consider two equilibria for the weak acid HX and its salt MX. The solubility product is

$$K_{sp} = [M^+][X^-]$$

The reaction involved is

$$HX(aq) \rightleftharpoons H^+(aq) + X^-(aq)$$

$$K_a = \frac{[H^+][X^-]}{[HX]}$$

Therefore,

$$\frac{[X^-]}{[HX]} = \frac{K_a}{[H^+]}$$

Taking inverse of both sides and adding 1, we get

$$\frac{[HX]}{[X^-]} + 1 = \frac{[H^+]}{K_a} + 1$$

or

$$\frac{[HX]+[X^-]}{[X^-]} = \frac{[H^+]+K_a}{K_a}$$

Taking reciprocal of the expression again, we get

$$\frac{[X^-]}{[HX]+[X^-]} = \frac{K_a}{[H^+]+K_a}$$

Replacing the concentration term on LHS with any variable, say *f*, we see that *f* increases as pH decreases. Substituting in the expression for solubility, we get

$$K_{sp} = [S][fS] = S^2\left(\frac{K_a}{K_a+[H^+]}\right)$$

or

$$K_{sp} = [S][fS] = S^2\left(\frac{K_a}{K_a+[H^+]}\right)$$

$$S = \left[\left(\frac{K_a+[H^+]}{K_a}\right)K_{sp}\right]^{1/2} \qquad (10.33)$$

The expression shows that the solubility increases with increase in $[H^+]$ or decreases in pH.

Solved Example 10-51

The pH at which $Mg(OH)_2$ begins to precipitate from a solution containing 0.10 M Mg^{2+} ions will be [K_{sp} of $Mg(OH)_2 = 1 \times 10^{-11}$]

Solution

When $Mg(OH)_2$ starts precipitation, the solubility product is $K_{sp} = [Mg^{2+}][OH^-]^2$

$$[0.1][OH^-]^2 = 1\times 10^{-11}$$

or

$$[OH^-] = 10^{-5}\ M$$

Thus, pOH = 5 and pH = 14 – pOH = 14 – 5 = 9.

10.17 | PREFERENTIAL PRECIPITATION OF SALTS

Selective precipitation means causing one metal ion to precipitate while holding another in solution. It occurs when more than one ion capable of forming a ppt. With another ion which is added to the solution. Often this is possible because of large differences in the solubilities of salts that we would generally consider to be insoluble. For example, the K_{sp} values for AgCl and $PbCl_2$ are 1.8×10^{-10} and 1.7×10^{-5}, respectively, which gives them molar solubilities in water of 1.3×10^{-5} M for AgCl and 1.6×10^{-2} M for $PbCl_2$. In terms of molar solubilities, lead chloride is approximately 1200 times more soluble in water than AgCl. If we had a solution containing both 0.10 M Pb^{2+} and 0.10 M Ag^+ and began adding Cl^-, AgCl would precipitate first (Fig. 10.11). In fact, we can calculate that before any $PbCl_2$ starts to precipitate, the concentration of Ag^+ will have been reduced to 1.4×10^{-8} M. Thus, nearly all the silver is removed from the solution without precipitating any of the lead, and the ions are effectively separated. All we need to do is find a way of adjusting the concentration of the Cl^- to achieve the separation.

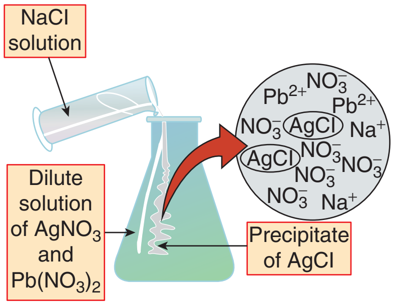


Figure 10.11 Selective precipitation.

In a solution containing Cl^-, Br^- and I^-, if Ag^+ ions are added then among the three, the least soluble silver salt is precipitated first. If the addition of Ag^+ ions is continued, eventually the salt having higher solubility and consequently the one having highest solubility get precipitated.

1. If the stoichiometry of the precipitated salts is the same, then the salts are precipitated in increasing order of K_{sp}.
2. If the stoichiometry of the precipitated salts is not the same, then with K_{sp} alone, we cannot predict the ion that will get precipitated first.

Consider a solution of Cl^- and CrO_4^{2-}. Both of these ions precipitate with Ag^+ and K_{sp} (AgCl) > K_{sp} (Ag_2CrO_4). It is found, however, that AgCl (less soluble) gets precipitated first when Ag^+ ions are added to the solution. By calculating the concentration of Ag^+ ion required to start precipitating through the K_{sp} and given concentration of Cl^- and CrO_4^{2-}, we find that $[Ag^+] > [Cl^-]$. Hence as $AgNO_3$ is added to the solution, the minimum of the two concentrations of Ag^+ to start the precipitating will be reached first, and thus the corresponding ion (Cl^-) will be precipitated in preference to the other. During precipitation, concentration of Cl^- decreases and that of Ag^+ increases till the time both the concentrations are equal. At this stage, the whole of Cl^- ions have been precipitated and the addition of more of $AgNO_3$ causes the precipitation of both the ions together.

1. Solubility of a salt of weak acid and strong base in basic buffer suppresses ionization as compared to pure water due to common ion effect. However, in acidic buffer solution, solubility increases more than pure water.
2. Solubility of salt of weak acid and weak base in pure water can be studied as follows. Let the solubility of salt be S, and y mol L^{-1} is the amount of salt getting hydrolyzed.

$$CH_3COONH_4 \rightleftharpoons \underset{S-y}{CH_3COO^-} + \underset{S-y}{NH_4^+} \tag{10.34}$$

$$\underset{S-y}{CH_3COO^-} + \underset{S-y}{NH_4^+} + H_2O \rightleftharpoons \underset{y}{CH_3COOH} + \underset{y}{NH_4OH} \tag{10.35}$$

The solubility product is $K_{sp} = (S-y)(S-y) = (S-y)^2$

Due to hydrolysis of salt from Eq. (10.34)

$$K_h = \frac{[CH_3COOH][NH_4OH]}{[CH_3COO^-][NH_4^+]} = \frac{y \cdot y}{(S-y)(S-y)} = \left(\frac{y}{S-y}\right)$$

and we also know that $K_h = \dfrac{K_w}{K_a K_b}$

3. Solubility of a salt of weak acid and weak base in acidic buffer can be studied as follows. Let the solubility of salt be S and y be the amount of weak acid being formed.

$$CH_3COONH_4 \rightleftharpoons \underset{S-y}{CH_3COO^-} + \underset{y}{NH_4^+}$$

$$\underset{(S-y)}{CH_3COO^-} + \underset{\text{(from acidic buffer)}}{H^+} \rightarrow \underset{y}{CH_3COOH} \qquad (10.36)$$

The solubility product is $\quad K_{sp} = [CH_3COO^-] + [NH_4^+][S-y][y] = y[S-y]$

For Eq. (10.36), we have $\quad \dfrac{1}{K_{a(CH_3COOH)}} K'_a = \dfrac{[CH_3COOH]}{[CH_3COO^-][NH_4^+]} = \dfrac{y}{(S-y)[H^+]}$

Solubility of CH_3COONH_4 in acidic buffer would be higher than in pure water.

4. Solubility of a salt of weak acid and weak base in basic buffer can be studied as follows.

$$CH_3COONH_4 \rightleftharpoons \underset{y}{CH_3COO^-} + \underset{S-y}{NH_4^+}$$

$$\underset{S-y}{NH_4^+} + \underset{\text{(from buffer)}}{OH^-} \rightleftharpoons \underset{y}{NH_4OH} \qquad (10.37)$$

The solubility product is $\quad K_{sp(CH_3COONH_4)} = [CH_3COO^-][NH_4^+] = y(S-y)$

Now, from Eq. (10.37), we have $\quad \dfrac{1}{K_b} K'_b = \dfrac{[NH_4OH]}{[NH^+][OH^-]} = \dfrac{y}{(S-y)[OH^-]}$

The solubility of CH_3COONH_4 in basic buffer would be higher than pure water.

Note: Solubility of AgCl in an aqueous solution containing NH_3
Let the amount of NH_3 initially be x M. If the solubility of salt be y mol L^{-1}.

$$\begin{array}{lcccc} & AgCl(s) & \rightleftharpoons & Ag^+ & + Cl^- \\ \text{Initial moles} & 0 & & y & 0 \\ \text{Moles at time,} & t & & b-y & y \end{array}$$

$$\underset{b-y}{Ag^+} + \underset{a-2y}{2NH_3} \rightleftharpoons \underset{y}{[Ag(NH_3)_2]^+(aq)}$$

where y is the amount of Ag^+ which reacted with NH_3.

$$K_{sp} = [Ag^+][Cl^-] = (b-y)y$$

After knowing the value of K_{sp} and K_b the value of solubility can be calculated.

Solved Example 10-52

Consider a solution containing Hg^{2+} and Fe^{2+}, both at molarities of 0.010 M. It is to be saturated with H_2S. Calculate the highest pH that this solution could have that would keep Fe^{2+} in solution while causing Hg^{2+} to precipitate as HgS.

Solution

Fe^{2+} is much more soluble in acid than Hg^{2+}. We want to make the H^+ concentration large enough to prevent FeS from precipitating, but small enough that HgS precipitates. First, we calculate the highest pH at which FeS will remain soluble, by using K_{spa} for FeS. (Recall that a saturated solution of $H_2S = 0.10$ M.)

$$K_{spa} = \frac{[Fe^{2+}][H_2S]}{[H^+]^2} = \frac{[0.010][0.10]}{[H^+]^2} = 6 \times 10^2$$

which gives $[H^+] = 0.0013$ M and pH = –log $[H^+] = 2.9$. Since Fe^{2+} is much more soluble in acid than Hg^{2+}, we already know that this pH will precipitate HgS, but we can check it by using K_{spb} for HgS.

$$K_{spb} = \frac{[Hg^{2+}][H_2S]}{[H^+]^2} = \frac{[0.010][0.10]}{[H^+]^2} = 2 \times 10^{-32}$$

which gives $[H^+] = 2.2 \times 10^{14}$ M. (This concentration is impossibly high, but it tells us that this much acid would be required to dissolve HgS at these concentrations.)

Solved Example 10-53

A solution contains a mixture of Ag^+ (0.10 M) and Hg_2^{2+} (0.10 M) which are to be separated by selective precipitation. Calculate the maximum concentration of iodide ion at which one of them gets precipitated almost completely. What % of that metal ion is precipitated? **(IIT-JEE 1984)**

Solution

For the precipitation, the ionic product should be greater than solubility product. Also, K_{sp} of $Hg_2I_2 = 2.5 \times 10^{-26}$ is much less than that of $AgI = 8.5 \times 10^{-17}$.

For the reaction $Hg_2I_2 \rightleftharpoons Hg_2^{2+} + 2I^-$, the solubility product is $K_{sp} = [Hg_2^{2+}][I^-]^2 = 2.5 \times 10^{-26}$

$$\text{Therefore, } [I^-] = \sqrt{\frac{K_{sp}}{[Hg_2^{2+}]}} = \sqrt{\frac{2.5 \times 10^{-26}}{0.1}} = 5.0 \times 10^{-13} \text{ M}$$

For the reaction $AgI \rightleftharpoons Ag^+ + 2I^-$, the solubility product is $K_{sp} = [Ag^+][I^-] = 8.5 \times 10^{-17}$

$$\text{Therefore, } [I^-] = \frac{K_{sp}}{[Ag^+]} = \frac{8.5 \times 10^{-17}}{0.1} = 8.5 \times 10^{-16} \text{ M}$$

On comparing, we find that $[I^-]$ required to precipitate AgI is less than that required to precipitate Hg_2I_2. So, AgI starts precipitating first and Hg_2I_2 gets precipitated only when $[I^-]$ reaches 5.0×10^{-13} M. The concentration of AgI left when Hg_2I_2 starts precipitating is

$$\frac{K_{sp} \text{ of AgI}}{[I^-] \text{ for } Hg_2I_2} = \frac{8.5 \times 10^{-17}}{5.0 \times 10^{-13}} = 1.7 \times 10^{-4} \text{M}$$

Therefore,

$$\% \text{ of } [Ag^+] \text{ precipitated} = \frac{1.7 \times 10^{-4}}{0.1} \times 100 = 0.17\%$$

So, the % of Ag^+ precipitated is 100 – 0.17 = 99.83%.

Solved Example 10-54

What range of pH would permit the selective precipitation of Cu^{2+} as $Cu(OH)_2$ from a solution that contains 0.10 M Cu^{2+} and 0.10 M Mn^{2+}? For $Mn(OH)_2$, $K_{sp} = 1.6 \times 10^{-13}$ and for $Cu(OH)_2$, $K_{sp} = 4.8 \times 10^{-20}$.

Solution

The reaction is $Cu(OH)_2(s) \rightleftharpoons Cu^{2+}(aq) + 2\,OH^-(aq)$. The solubility product is

$$K_{sp} = [Cu^{2+}][OH^-]^2 \Rightarrow 4.8 \times 10^{-20} = (0.10)[OH^-]^2$$

Solving, we get $[OH^-] = 6.9 \times 10^{-10}$ M
Now, pOH = –log $[OH^-]$ = –log$[6.9 \times 10^{-10}]$ = 9.2 and
pH = 14.00 –pOH = 4.8.

So, 4.8 is the pH *below* which all the $Cu(OH)_2$ will be soluble.

For the reaction $Mn(OH)_2(s) \rightleftharpoons Mn^{2+}(aq) + 2OH^-(aq)$, the solubility product is

$$K_{sp} = [Mn^{2+}][OH^-]^2 \Rightarrow 1.6 \times 10^{-13} = (0.10)[OH^-]^2$$

Solving, we get $[OH^-] = 1.3 \times 10^{-6}$ M
Now, pOH = –log$[OH^-]$ = –log$[1.3 \times 10^{-6}]$ = 5.9 and
pH = 14.00 –pOH = 8.1

So, 8.1 is the pH below which all the $Mn(OH)_2$ will be soluble.

Therefore, from pH = 4.8 – 8.1 $Mn(OH)_2$ will be soluble, but some $Cu(OH)_2$ will precipitate out of solution.

Solved Example 10-55

Given $K_{sp(AgCl)} = 1.8 \times 10^{-10}$, $K_{sp(AgBr)} = 5 \times 10^{-13}$ and $K_{sp(AgI)} = 8.3 \times 10^{-17}$.

A solution contains $[I^-] = [Br^-] = [Cl^-] = 0.1$ M each. Calculate:

(a) The minimum $[Ag^+]$ concentration to precipitate (i) AgI, (ii) AgBr and (iii) AgCl

(b) The minimum $[Ag^+]$ required to precipitate (i) AgI only and (ii) AgI and AgBr only.

(c) The percentage of $[I^-]$ unreacted when AgBr first precipitates.

Solution

(a) The minimum concentration required for precipitation of salts is:

(i) $K_{sp(AgI)} = [Ag^+][I^-]$

Therefore,

$$[Ag^+] = \frac{K_{sp(AgI)}}{[I^-]} = \frac{8.3 \times 10^{-17}}{0.1}$$

$$[Ag^+] > 8.3 \times 10^{-16}$$

(ii) $K_{sp(AgBr)} = [Ag^+][Br^-]$

Therefore,

$$[Ag^+] = \frac{K_{sp(AgBr)}}{[Br^-]} = \frac{5 \times 10^{-13}}{0.1}$$

$$[Ag^+] > 5 \times 10^{-12}$$

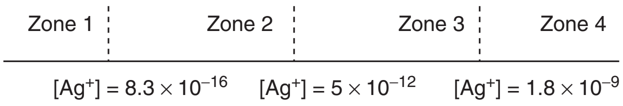
(iii) $K_{sp(AgCl)} = [Ag^+][Cl^-]$

Therefore,

$$[Ag^+] = \frac{K_{sp(AgCl}}{[Cl^-]} = \frac{1.8 \times 10^{-10}}{0.1}$$

$$[Ag^+] > 1.8 \times 10^{-9}$$

(b) Consider the following distribution of precipitating ions in different zones:



In Zone 1: AgI, AgBr, AgCl are all not precipitated.

In Zone 2: Only AgI is precipitated.

In Zone 3: Both AgI and AgBr are precipitated.

In Zone 4: All are precipitated.

(i) Maximum $[Ag^+]$ at which AgI only is precipitated = 5×10^{-12} M.

(ii) Maximum$[Ag^+]$ at which both AgI and AgBr are precipitated =1.8×10^{-9} M.

(**Note:** For precipitation, ionic product > K_{sp})

(c) When AgBr first precipitates, $[Ag^+] > 5 \times 10^{-12}$ M. Therefore, $[I^-]$ unreacted at this point can be calculated as

$$K_{sp(AgI)} = [Ag^+][I^-]_{unreacted}$$

$$8.3 \times 10^{-17} = [5 \times 10^{-12}][I^-]_{unreacted}$$

$$[I^-]_{unreacted} = 1.66 \times 10^{-5}$$

$$\%[I^-]_{unreacted} = \frac{1.66 \times 10^{-5}}{0.1} \times 100 = 0.0166\%$$

$$\%[I^-]_{reacted} = 99.9834\%$$

This shows that when AgBr first precipitates, most of [AgI] has already been precipitated. This makes logical sense, as per the K_{sp} values of AgI and AgBr.

10.18 | APPLICATIONS OF SOLUBILITY PRODUCT

The important applications of solubility product are listed as follows:

1. **Qualitative salt analysis:** As discussed in Section, selective precipitation of one metal ion while keeping other in the solution can be achieved due to large difference in the solubility of the salt formed with the precipitation reagent. This principle is used in qualitative salt analysis of mixture of radicals. Some important reactions are:
   (a) Precipitation of Group I radicals (Pb^{2+}, Ag^+ and Hg_2^{2+})as chlorides with diluted HCl.
   (b) Precipitation of Group II radicals ($Cu^{2+}, Sn^{2+}, Cd^{2+}\ Hg^{2+}, As^{3+}, Sb^{3+}, Bi^{3+}, As^{5+}, Sb^{5+}, Sn^{4+}$) by H_2S in presence of HCl

- **(c)** Precipitation of Group III radicals (Al^{3+}, Cr^{3+}, Fe^{3+}) with NH_4OH in presence of NH_4Cl.
- **(d)** Precipitation of Group IV (Ni^{2+}, Co^{2+}, Mn^{2+}, Zn^{2+}) elements with H_2S in presence of NH_4OH.
- **(e)** Precipitation of Group V elements (Ca^{2+}, Sr^{2+}, Ba^{2+}) with $(NH_4)_2CO_3$ in presence of NH_4OH.

2. **Purification of common salt:** In the purification process, HCl gas is passed through the saturated salt solution, which causes pure NaCl to precipitate out. The increased concentration of chloride ions causes the equilibrium to shift in the backward direction.

$$NaCl(s) \rightleftharpoons Na^+(aq) + Cl^-(aq)$$

The product of ionic concentration is more that solubility constant, so precipitation occurs.

3. **Preparation of sodium bicarbonate:** In Solvay process, $NaHCO_3$ is precipitated by the addition of NH_4HCO_3.
4. **Precipitation of soap:** Soap is salted out of saturated soap solution (RCOONa) of higher fatty acids by addition of sodium chloride.

SOLVED OBJECTIVE QUESTIONS FROM PREVIOUS YEAR PAPERS

1. HX is a weak acid ($K_a = 10^{-5}$). It forms a salt NaX (0.1 M) on reaction with caustic soda. The degree of hydrolysis of NaX is **(IIT-JEE 2003)**

(A) 0.01%
(B) 0.0001%
(C) 0.1%
(D) 0.5%

Solution

(A) The reaction is NaX + $H_2O \rightarrow$ NaOH + HX. The hydrolysis constant is

$$K_h = \frac{K_w}{K_a} = 10^{-9}$$

Now, $K_h = Ch^2 = 10^{-9}$ where h is the degree of hydrolysis and $C = 0.1$ M. Solving, we get

$$h^2 = 10^{-8} \Rightarrow h = 10^{-4}$$

$$\alpha = 10^{-4}$$

Therefore, %hydrolysis = 0.01%.

2. 0.1 mol of CH_3NH_2 ($K_b = 6 \times 10^{-4}$) is added to 0.08 mol of HCl and the solution is diluted to 1 L. The hydrogen ion concentration in the solution is **(IIT-JEE 2005)**

(A) 5×10^{-5} M
(B) 8×10^{-2} M
(C) 1.6×10^{-11} M
(D) 6.7×10^{-11} M

Solution

(D) The reaction is

	CH_3NH_2 +	HCl $\rightarrow$	$CH_3\overset{+}{N}H_2$ +	Cl^-
Initial concentration	0.1	0.08	0	0
Concentration in solution	0.02			0.08

The concentrations of $[OH^-]$ and $[H^+]$ are

$$[OH^-] = \frac{K_b[CH_3NH_2]}{[CH_3\overset{+}{N}H_3]} = \frac{6 \times 10^{-4} \times 0.02}{0.08} = \frac{3}{2} \times 10^{-4}$$

$$[H^+] = \frac{K_w}{[OH^-]} = 0.666 \times 10^{-10} = 6.7 \times 10^{-11}$$

3. $Ag^+ + NH_3 \rightleftharpoons [Ag(NH_3)]^+$; $K_1 = 3.5 \times 10^{-3}$
$[Ag(NH_3)]^+ + NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$; $K_2 = 1.7 \times 10^{-3}$ then the formation constant of $[Ag(NH_3)_2]^+$ is **(IIT-JEE 2006)**

(A) 6.08×10^{-6}
(B) 6.08×10^{6}
(C) 6.08×10^{-9}
(D) None of these

Solution

(A) Given that

$$Ag^+ + NH_3 \rightleftharpoons [Ag(NH_3)^+]$$

$$K_1 = \frac{[Ag(NH_3)^+]}{[Ag^+][NH_3]} = 3.5 \times 10^{-3}$$

and

$$[Ag(NH_3)]^+ + NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$$

$$K_2 = \frac{[Ag(NH_3)_2]^+}{[Ag(NH_3)]^+[NH_3]} = 1.7 \times 10^{-3}$$

Therefore, for the overall reaction

$$Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$$

$$K = \frac{[Ag(NH_3)_2]^+}{[Ag^+][NH_3]^2} = \frac{[Ag(NH_3)^+]}{[Ag^+][NH_3]} \times \frac{[Ag(NH_3)_2]^+}{[Ag(NH_3)]^+[NH_3]}$$

$$= K_1 \cdot K_2 = 3.5 \times 10^{-3} \times 1.73 \times 10^{-3} = 6.08 \times 10^{-6}$$

4. The species present in solution when CO_2 is dissolved in water are **(IIT-JEE 2006)**

(A) CO_2, H_2CO_3, HCO_3^-, CO_3^2
(B) H_2CO_3, CO_3^{2-}
(C) CO_3^{2-}, HCO_3^-
(D) CO_2, H_2CO_3

Solution

(A) The reactions involved are

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$
$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$
$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$$

5. 2.5 mL of (2/5) M weak monoacidic base ($K_b = 1 \times 10^{-12}$ at 25°C) is titrated with (2/15) M HCl in water at 25°C. The concentration of H^+ at equivalence point is ($K_w = 1 \times 10^{-14}$ at 25°C) **(IIT-JEE 2008)**

(A) 3.7×10^{-13} M (B) 3.2×10^{-7} M
(C) 3.2×10^{-2} M (D) 2.7×10^{-2} M

Solution

(D) The reactions involved are

$$BOH + HCl \rightarrow BCl + H_2O$$

	$B^+ + H_2O$	$\rightleftharpoons BOH$	$+ H^+$
Initial moles	C	α	α
Moles at equilibrium	$C - C\alpha$	$C\alpha$	$C\alpha$

Using $M_1V_1(\text{BOH}) = M_2V_2(\text{HCl})$, we get

$$2.5 \times \frac{2}{5} = \frac{2}{15} \times V_2 \Rightarrow V_2 = 7.5 \text{ mL}$$

Also, we have $M_1V_1(\text{salt}) = M_2V_2$ (BOH), that is,

$$M_1 \times (2.5 + 7.5) = 2.5 \times \frac{2}{5} \Rightarrow M_1 = 0.1 \text{ M}$$

Now, $K_a \times K_b = K_w$ where $K_a = C\alpha^2/(1 - a)$. Therefore,

$$\frac{K_w}{K_b} = 0.1 \times \frac{\alpha^2}{1 - \alpha} \Rightarrow \alpha = 0.27$$

Hence, $[H^+] = C\alpha = 2.7 \times 10^{-2}$ M.

6. Solubility product constants (K_{sp}) of salts of types MX, MX_2 and M_3X at temperature T are 4.0×10^{-8} M, 3.2×10^{-14} M and 2.7×10^{-15} M, respectively. Solubilities (mol dm^{-3}) of the salts at temperature T are in the order **(IIT-JEE 2008)**

(A) $MX > MX_2 > M_3X$ (B) $M_3X > MX_2 > MX$
(C) $MX_2 > M_3X > MX$ (D) $MX > M_3X > MX_2$

Solution

(D) The solubilities are calculated as

$$\text{Solubility of MX} = (4 \times 10^{-8})^{1/2} = 2 \times 10^{-4}$$

$$\text{Solubility of } MX_2 = (3.2 \times 10^{-14})^{1/3} = 3.17 \times 10^{-5}$$

$$\text{Solubility of } MX_3 = (2.7 \times 10^{-15})^{1/4} = 2.27 \times 10^{-4}$$

So, $MX > M_3X > MX_2$.

7. The dissociation constant of a substituted benzoic acid at 25°C is 1.0×10^{-4}. The pH of a 0.01 M solution of its sodium salt is _______. **(IIT-JEE 2009)**

Solution

(8) Given that K_a (C_6H_5COOH) = 1×10^{-4} and pH of 0.01 M C_6H_5COONa is to be calculated. The reaction can be expressed as

	$C_6H_5COO^- + H_2O \rightleftharpoons$	C_6H_5COOH	$+ OH^-$
Initial moles	0.01	0	0
Moles at equilibrium	$0.01(1 - h)$	$0.01h$	$0.01h$

The hydrolysis constant is given by

$$K_h = \frac{K_w}{K_a} = \frac{0.01h^2}{1 - h} \Rightarrow \frac{10^{-14}}{10^{-4}} = \frac{10^{-2}h^2}{1 - h}$$

Now, $1 - h$ is approximately equal to 1, so

$h = (10^{-14+4+2})^{1/2}\ 10^{-4}$. Hence,

$$[OH^-] = 0.01h = 0.01 \times 10^{-4} = 10^{-6} \text{ M} \quad \text{and}$$

$$[H^+] = \frac{10^{-14}}{10^{-6}} = 10^{-8} \text{ M}$$

Therefore, pH = 8.

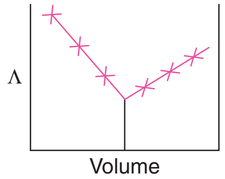
8. Aqueous solutions of HNO_3, KOH, CH_3COOH and CH_3COONa of identical concentrations are provided. The pair(s) of solutions which form a buffer upon mixing is(are) **(IIT-JEE 2010)**

(A) HNO_3 and CH_3COOH
(B) KOH and CH_3COONa
(C) HNO_3 and CH_3COONa
(D) CH_3COOH and CH_3COONa

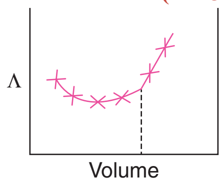
Solution

(C, D) In (C), if HNO_3 is present in limiting amount then this mixture will be a buffer and in (D), the mixture contains a weak acid, that is, acetic acid and its salt of strong base, that is, sodium acetate.

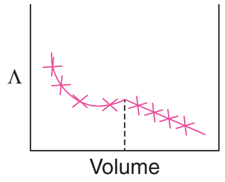
9. $AgNO_3$(aq) was added to an aqueous KCl solution gradually and the conductivity of the solution was measured. The plot of conductance (Λ) vs. the volume of $AgNO_3$ is **(IIT-JEE 2011)**



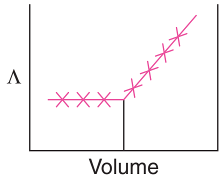
(P)



(Q)



(R)



(S)

(A) P (B) Q
(C) R (D) S

Solution

(D) The plot is shown in Fig. 10.12.
The reaction involved is

$$AgNO_3(aq) + K^+Cl^-(aq) \rightleftharpoons AgCl(s) + KNO_3^-$$

On adding $AgNO_3$, the precipitation will not start immediately unless and until the ionic product of AgCl exceeds the solubility product. After that $AgNO_3$ will be precipitated in the form of AgCl and also at the same time NO_3^- ions will be added to the solution. Since now the number of ions remains the same that is why the conductance also remains the same (shown in Fig. 10.12 by line AB). After the precipitation is complete, on further adding $AgNO_3$ the number of ions will now increase, and hence the conductance will also increase (shown by line BC).

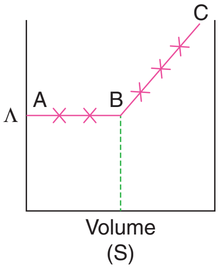


Figure 10.12

10. In 1 L saturated solution of AgCl [K_{sp} (AgCl) = 1.6×10^{-10}], 0.1 mol of CuCl [K_{sp} (CuCl) = 1.0×10^{-6}] is added. The resultant concentration of Ag^+ in the solution is 1.6×10^{-n}]. What is the value of n? **(IIT-JEE 2011)**

Solution

(7) The reaction involved is

$$AgCl(s) \rightleftharpoons \underset{x}{Ag^+} + \underset{x}{Cl^-}$$

$$CuCl(s) \rightleftharpoons \underset{y}{Cu^+} + \underset{y}{Cl^-}$$

Net Cl^- in solution = $(x + y)$. Now, the solubility product of AgCl is $K_{sp}(AgCl) = 1.6 \times 10^{-10} = [Ag^+][Cl^-] = x(x+y)$

or $$x(x+y) = 1.6 \times 10^{-10} \qquad (1)$$

Now, the solubility product of CuCl is

$$K_{sp}(CuCl) = 1.0 \times 10^{-6} = [Cu^+][Cl^-]$$

or $$y(x+y) = 1.0 \times 10^{-6} \qquad (2)$$

Dividing Eq. (1) by Eq. (2), we get

$$\frac{x}{y} = \frac{1.6 \times 10^{-10}}{1.0 \times 10^{-6}} = 1.6 \times 10^{-4} \Rightarrow y = \frac{10^4}{1.6}$$

Putting this value of y in Eq. (1), we get

$$x \times \left(x + \frac{10^4}{1.6}x\right) = 1.6 \times 10^{-10}$$

or $$x^2 = (1.6)^2 \times 10^{-14} \approx 1.6 \times 10^{-14}$$

or $x = 1.6 \times 10^{-7} = [Ag^+]$. Therefore, $n = 7$.

11. The initial rate of hydrolysis of methyl acetate (1 M) by a weak acid (HA, 1 M) is 1/100th of that of a strong acid (HX, 1M), at 25°C. The K_a of HA is **(JEE Advanced 2013)**

(A) 1×10^{-4}
(B) 1×10^{-5}
(C) 1×10^{-6}
(D) 1×10^{-3}

Solution

(A) The rate with respect to weak acid is

$$rate_1 = k[H^+]_{weak}[Ester]$$

and rate with respect to strong acid is

$$rate_2 = k[H^+]_{strong}[Ester]$$

Now, given that $[H^+]_{weak} = \dfrac{[H^+]_{strong}}{100} = \dfrac{1}{100} = 0.01$ M

The reaction involved is

$$\underset{1-0.01\approx1}{HA} \rightleftharpoons \underset{0.01}{H^+} + \underset{0.01}{A^-}$$

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{0.01 \times 0.01}{1} = 10^{-4}$$

12. The K_{sp} of Ag_2CrO_4 is 1.1×10^{-12} at 298 K. The solubility (in mol/L) of Ag_2CrO_4 in a 0.1 M $AgNO_3$ solution is **(JEE Advanced 2013)**

(A) 1.1×10^{-11}
(B) 1.1×10^{-10}
(C) 1.1×10^{-12}
(D) 1.1×10^{-9}

Solution

(B) The reaction involved is

$$\underset{S}{Ag_2CrO_4} \rightleftharpoons \underset{0.1+2S\approx0.1}{2Ag^+} + \underset{S}{CrO_4^{2-}}$$

The solubility product is
$$K_{sp} = [Ag^+]^2[CrO_4^{2-}] \Rightarrow \ 1.1 \times 10^{-12} = (0.1)^2 \times S$$

Therefore, $S = [CrO_4^{2-}] = \dfrac{1.1 \times 10^{-12}}{(0.1)^2} = 1.1 \times 10^{-10}\,\text{mol L}^{-1}$

Paragraph for Questions 13 and 14: When 100 mL of 1.0 M HCl was mixed with 100 mL of 1.0 M NaOH in an insulated beaker at constant pressure, a temperature increase of 5.7 °C was measured for the beaker and its contents (**Expt. 1**). Because the enthalpy of neutralization of a strong acid with a strong base is a constant (–57.0 kJ mol^{-1}), this experiment could be used to measure the calorimeter constant. In a second experiment (**Expt. 2**) 100 mL of 2.0 M acetic acid ($K_a = 2.0 \times 10^{-5}$) was mixed with 100 mL of 1.0 M NaOH (under identical conditions to **Expt. 1**) where a temperature rise of 5.6°C was measured. (Consider heat capacity of all solutions as 42 J g^{-1} K^{-1} and density of all solutions as 1.0 g mL^{-1}.)

13. Enthalpy of dissociation (in kJ mol^{-1}) of acetic acid obtained from the **Expt. 2** is **(JEE Advanced 2015)**

(A) 1.0
(B) 10. 0
(C) 24.5
(D) 51.4

Solution

(A) Energy evolved on neutralization of HCl and NaOH = 0.1 × 57 = 5.7 kJ = 5700 J
Energy utilized to rise the temperature of the solution = $ms \cdot \Delta T$ = 200 × 1 × 4.2 × 5.7 = 4788 J
Energy used to increase temperature of calorimeter = 5700 – 4788 = 912 J

$$ms \cdot \Delta T = 912$$

$m \times s \times 5.7 = 912 \Rightarrow ms = 160\ \text{J°C}^{-1}$ [Calorimeter constant]
Energy evolved by neutralization of CH_3COOH and NaOH = 200 × 4.2 × 5.6 + 160 × 5.6 = 5600 J

So, energy used in dissociation of 0.1 mol CH_3COOH = 5700 – 5600 = 100 J
Thus, enthalpy of dissociation = 1 $kJmol^{-1}$

14. The pH of the solution after **Expt. 2** is **(JEE Advanced 2015)**

(A) 2.8 (B) 4.7
(C) 5.0 (D) 7.0

Solution

(B) In **Expt. 2**, the final solution is a buffer as it contains equimolar amounts of acid and salt.

$$\text{pH} = \text{p}K_a + \log\frac{[\text{salt}]}{[\text{acid}]} \qquad (1)$$

$$\begin{aligned}\text{p}K_a &= -\log(2\times10^{-5})\\ &= -0.3010+5\\ &= 4.699 \approx 4.7\end{aligned}$$

$$[\text{Salt}] = [CH_3COONa] = \frac{100}{200}\times 2 = 1\text{ M}$$

$$[\text{Acid}] = [CH_3COOH] = \frac{200-100}{200}\times 2 = \frac{100}{200}\times 2 = 1\text{M}$$

Substituting the values in Eq. (1), we get

$$\begin{aligned}\text{pH} &= 4.7 + \log\frac{1}{1}\\ &= 4.7\end{aligned}$$

15. The solubility in water of a sparingly soluble salt AB_2 is 1.0×10^{-5} mol L^{-1}. Its solubility product number will be **(AIEEE 2003)**

(A) 4×10^{-15} (B) 4×10^{-10}
(C) 1×10^{-15} (D) 1×10^{-10}

Solution

(A) The solubility product is

$$K_{sp} = S(2S)^2 = 4S^3 = 4\times(1.0\times10^{-5})^3 = 4\times10^{-15}$$

16. Which one of the following statements is not true? **(AIEEE 2003)**

(A) The conjugate base of $H_2PO_4^-$ is HPO_4^{2-}
(B) pH + pOH = 14 for all aqueous solutions
(C) The pH of 1×10^{-8} M HCl is 8
(D) 96,500 coulombs of electricity when passed through $CuSO_4$ solution deposits 1 g equiv. of copper at the cathode.

Solution

(C) For acidic solution, pH should be less than 7.

17. The molar solubility product of a sparingly soluble salt (in mol L^{-1}) MX_4 is S. The corresponding solubility product K_{sp} S is given in terms of K_{sp} by the relation **(AIEEE 2004)**

(A) $S = \left(\frac{K_{sp}}{128}\right)^{1/4}$ (B) $S = \left(\frac{K_{sp}}{256}\right)^{1/5}$

(C) $S = (256K_{sp})^{1/5}$ (D) $S = (256K_{sp})^{1/4}$

Solution

(B) Consider the reaction: $MX_4 \rightleftharpoons \underset{S}{M^{4+}} + \underset{4S}{4X^-}$

The solubility product is

$$K_{sp} = S(4S)^4 = 256S^5 \Rightarrow S = \left(\frac{K_{sp}}{256}\right)^{1/5}$$

18. Hydrogen ion concentration in mol L^{-1} in a solution of pH = 5.4 will be **(AIEEE 2005)**

(A) 3.98×10^{8} (B) 3.88×10^{6}
(C) 3.68×10^{-6} (D) 3.98×10^{-6}

Solution

(D) The pH is pH = $-\log[H^+] \Rightarrow 5.4 = -\log[H^+]$.

So, $[H^+]$ = antilog (6.06) = 3.98×10^{-6}

19. The solubility product of a salt having general formula MX_2, in water is 4×10^{-12}. The concentration of M^{2+} ions in the aqueous solution of the salt is **(AIEEE 2005)**

(A) 2.0×10^{-6} M (B) 1.0×10^{-4} M
(C) 1.6×10^{-4} M (D) 4.0×10^{-10} M

Solution

(B) The reaction is $MX_2 \rightleftharpoons \underset{S}{M^{2+}} + \underset{2S}{2X^-}$. So,

$$K_{sp} = S(2S)^2 = 4S^3$$

or

$$S = \left(\frac{K_{sp}}{4}\right)^{1/3} = 1\times10^{-4}$$

20. Given the data at 25°C,

$$Ag + I^- \rightleftharpoons AgI + e^-;\ E^\circ = 0.152\text{ V}$$
$$Ag \rightleftharpoons Ag^+ + e^-;\ E^\circ = -0.800\text{ V}$$

What is the value of log K_{sp} for AgI? **(AIEEE 2006)**

(A) –8.12 (B) +8.612
(C) –37.83 (D) –16.13

Solution

(D) From Nernst equation, we have

$$E^\circ_{cell} = \frac{2.303RT}{nF}\log K_{sp} \qquad (1)$$

$$\begin{aligned}AgI + e^- &\rightleftharpoons Ag + I^-; E^\circ = -0.152\text{ V}\\ Ag &\rightleftharpoons Ag^+ + e^-;\ E^\circ = -0.800\text{ V}\\ \hline AgI(s) &\rightarrow Ag^+ + I^-; E^\circ = -0.952\end{aligned}$$

Substituting in Eq. (1), we have

$$-0.952 = \frac{0.059}{1}\log K_{sp} \Rightarrow \log K_{sp} = -\frac{0.952}{0.059} = -16.135$$

21. The first and second dissociation constants of an acid H_2A are 1.0×10^{-5} and 5.0×10^{-10}, respectively. The overall dissociation constant of the acid will be **(AIEEE 2007)**

(A) 0.2×10^{5} (B) 5.0×10^{5}
(C) 5.0×10^{15} (D) 5.0×10^{-15}

Solution

(D) Let us first consider the dissociation of H_2A and HA

$$H_2A \rightleftharpoons HA^- + H^+ \quad K_1 = \frac{[HA^-][H^+]}{[HA]}$$

$$HA^- \rightleftharpoons H^+ + A^{2-} \quad K_2 = \frac{[H^+][A^{2-}]}{[HA^-]}$$

For the reaction

$$H_2A \rightleftharpoons 2H^+ + A^{2-}$$

we have

$$K = \frac{[H^+]^2[A^{2-}]}{[H_2A]} = K_1 \times K_2 = 1\times10^{-5} \times 5\times10^{-10} = 5\times10^{-15}$$

22. In a saturated solution of the sparingly soluble strong electrolyte $AgIO_3$ (Molecular mass = 283 g mol^{-1}) the equilibrium which sets in is

$$AgIO_3(s) \rightleftharpoons Ag^+(aq) + IO_3^-(aq)$$

If the solubility product constant K_{sp} of $AgIO_3$ at a given temperature is 1.0×10^{-8}, what is the mass of $AgIO_3$ contained in 100 mL of its saturated solution? **(AIEEE 2007)**

(A) 1.0×10^{-4} g (B) 28.3×10^{-2} g
(C) 2.83×10^{-3} g (D) 1.0×10^{-7} g

Solution

(C) The reaction involved is

$$AgIO_3(s) \rightleftharpoons Ag^+ + IO_3^-$$

Let S be the solubility product of $AgIO_3$, then

$$K_{sp} = [Ag^+][IO_3^-]$$

$$\text{or} \quad 1.0\times10^{-8} = S^2 \Rightarrow S = 10^{-4} \text{ mol L}^{-1}$$

$$\text{or} \quad S = 10^{-4} \times 283 \times \frac{100}{1000} = 283\times10^{-5}$$

$$= 2.83\times10^{-3} \text{ g per 100 mL}$$

23. The pK_a of a weak acid (HA) is 4.5. The pOH of an aqueous buffered solution of HA in which 50% of the acid is ionized is **(AIEEE 2007)**

(A) 7.0 (B) 4.5
(C) 2.5 (D) 9.5

Solution

(D) For buffer solution (Henderson's equation)

$$pH = pK_a + \log\frac{[Salt]}{[Acid]} = 4.5 + \log\frac{[Salt]}{[Acid]}$$

As the acid is 50% ionized, which means that

$$[Salt] = [Acid]$$

$$pH = 4.5 + \log 1 = 4.5$$

Therefore, pOH = 14 – pH = 14 – 4.5 = 9.5

24. Regular use of which of the following fertilizers increases the acidity of soil? **(AIEEE 2007)**

(A) Ammonium sulphate
(B) Potassium nitrate
(C) Urea
(D) Superphosphate

Solution

(A) Ammonium sulphate is a salt of strong acid and weak base. On hydrolysis, it produces H^+ ions which increase the acidity of soil.

$$(NH_4)_2SO_4 \rightarrow 2NH_4^+ + SO_4^{2-}$$
$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$

25. Four species are listed below

(I) HCO_3^- (II) H_3O^+
(III) HSO_4^- (IV) HSO_3F

Which one of the following is the correct sequence of their acid strength? **(AIEEE 2008)**

(A) IV < II < III < I (B) II < III < I < IV
(C) I < III < II < IV (D) III < I < IV < II

Solution

(C) The order is (IV) > (II) > (III) > (I). This is because weaker the conjugate base, stronger is its conjugate acid.

26. The equilibrium constants K_{p_1} and K_{p_2} for the reactions $X \rightleftharpoons 2Y$ and $Z \rightleftharpoons P + Q$ respectively, are in the ratio of 1:9. If the degree of dissociation of X and Z be equal, then the ratio of total pressure at these equilibria is **(AIEEE 2008)**

(A) 1:36 (B) 1:1
(C) 1:3 (D) 1:9

Solution

(A) The reaction can be expressed as

	$X \rightleftharpoons$	$2Y$
Initial moles	1	0
Moles at equilibrium	$(1-\alpha)$	2α

For reaction (I), let the total pressure be equal to p. The total number of moles in reaction = $1 - x + 2x = 1 + x$.

For reaction (II), let the total pressure be equal to p'. The total number of moles in reaction = $1 - x + x + x = 1 + x$.

$$\text{Therefore,} \quad K_{p_1} = \frac{\left(\frac{2x}{1+x}p\right)^2}{\left(\frac{1-x}{1+x}p\right)} = \frac{4px^2}{1-x^2} \quad \text{and}$$

$$K_{p_2} = \frac{\left(\frac{x}{1+x}p'\right)\left(\frac{x}{1+x}p'\right)}{\left(\frac{1-x}{1+x}p'\right)} = \frac{p'x^2}{1-x^2}$$

Given that the ratio of $K_{p_1}/K_{p_2} = 1/9$, therefore,

$$\frac{K_{p_1}}{K_{p_2}} = \frac{1}{9} = \frac{\left(\dfrac{4p^2x^2}{1-x^2}\right)}{\left(\dfrac{p'x^2}{1-x^2}\right)^2} = \frac{4p}{p'}$$

or
$$\frac{p}{p'} = \frac{1}{36}$$

27. The pK_a of a weak acid, HA, is 4.80. The pK_b of a weak base, BOH, is 4.78. The pH of an aqueous solution of the corresponding salt, BA, will be **(AIEEE 2008)**

(A) 9.58 (B) 4.79 (C) 7.01 (D) 9.22

Solution

(C) The reaction is

$$\begin{array}{l} BA \rightleftharpoons B^+ + A^- \xrightarrow{H_2O} AH + OH^- \\ \qquad\quad \downarrow H_2O \\ \qquad BOH + H^+ \end{array}$$

Now since,

$$[H^+] = \sqrt{\frac{K_w + K_a}{K_b}} = 7 + \frac{1}{2}pK_a - \frac{1}{2}pK_b$$

Therefore, $\quad pH = 7.01$

28. Solid $Ba(NO_3)_2$ is gradually dissolved in a 1.0×10^{-4} M Na_2CO_3 solution. At what concentration of Ba^{2+} will a precipitate begin to form? (Given K_{sp} for $BaCO_3 = 5.1 \times 10^{-9}$.) **(AIEEE 2009)**

(A) 8.1×10^{-8} M (B) 8.1×10^{-7} M
(C) 4.1×10^{-5} M (D) 5.1×10^{-5} M

Solution

(D) The reaction is

$$Ba(NO_3)_2 + CaCO_3 \rightleftharpoons BaCO_3 + 2NaNO_3$$

Here $[CO_3^{2-}] = [Na_2CO_3] = 10^{-4}$ M. Therefore, the solubility product is

$$K_{sp} = [Ba^{2+}][CO_3^{\,2-}]$$

or
$$5.1 \times 10^{-9} = [Ba^{2+}] \times 10^{-4}$$

we get $[Ba^{2+}] = 5.1 \times 10^{-5}$. At this value, precipitation just starts.

29. Three reactions involving $H_2PO_4^-$ are given below;

(I) $H_3PO_4 + H_2O \rightarrow H_3O^+ + H_2PO_4^-$
(II) $H_2PO_4^- + H_2O \rightarrow HPO_4^{2-} + H_3O^+$
(III) $H_2PO_4^- + OH^- \rightarrow H_3PO_4 + O^{2-}$

In which of the above does $H_2PO_4^-$ act as an acid? **(AIEEE 2010)**

(A) (I) only (B) only
(C) (I) and (II) (D) (III) only

Solution

(B) (I) $\underset{\text{Acid}}{H_3PO_4} + H_2O \rightarrow H_3O^+ + \underset{\text{Conjugate base}}{H_2PO_4^-}$

(II) $\underset{\text{Acid}}{H_2PO_4^-} + H_2O \rightarrow \underset{\text{Conjugate base}}{HPO_4^{2-}} + H_3O^+$

(III) $\underset{\text{Base}}{H_2PO_4^-} + OH^- \rightarrow \underset{\text{Conjugate acid}}{H_3PO_4} + O^{2-}$

30. In aqueous solution the ionization constants for carbonic acid are $K_1 = 4.02 \times 10^{-7}$ and $K_2 = 4.8 \times 10^{-11}$. Select the correct statement for a saturated 0.034 M solution of the carbonic acid **(AIEEE 2010)**

(A) The concentration of H^+ is double that of CO_3^{2-}.
(B) The concentration of CO_3^{2-} is 0.034 M.
(C) The concentration of CO_3^{2-} is greater than of HCO_3^-
(D) The concentrations of H^+ and HCO_3^- are approximately equal.

Solution

(D) The reactions are

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \quad K_1 = 4.2 \times 10^{-7} \qquad (1)$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \quad K_2 = 4.8 \times 10^{-11} \qquad (2)$$

As $K_2 \ll K_1$. All the H^+ ions (in total) are due to Eq. (1) only.
From the first equation,

$$[H^+] = [HCO_3^{\,-}] = [H^+]_{total}$$

$[CO_3^{2-}]$ is negligible as compared to $[HCO_3^{2-}]$ or $[H^+]_{total}$. So, the concentrations of H^+ and HCO_3^- are approximately equal.

31. The correct order of increasing basicity of the given conjugate ($R = CH_3$) is **(AIEEE 2010)**

(A) $RCO\bar{O} < HC = \bar{C} < \bar{N}H_2 < \bar{R}$

(B) $RCO\bar{O} < HC = \bar{C} < \bar{R} < \bar{N}H_2$

(C) $\bar{R} < HC = \bar{C} < RCO\bar{O} < \bar{N}H_2$

(D) $RCO\bar{O} < \bar{N}H_2 < HC = \bar{C} < \bar{R}$

Solution

(A) Because strong acids have weak conjugate base and RCOOH being the strongest acid among these has the weakest conjugate base.

32. Solubility product of silver bromide is 5.0×10^{-13}. The quantity of potassium bromide(molar mass taken as 120 g mol^{-1} to be added to 1 L of 0.05 M solution of silver nitrate to start the precipitation of AgBr is **(AIEEE 2010)**

(A) 5.0×10^{-8} g (B) 1.2×10^{-10} g
(C) 1.2×10^{-9} g (D) 6.2×10^{-5} g

Solution

(C) The reaction involved is $\mathrm{Ag^+ + Br^- \rightleftharpoons AgBr}$ Precipitation will start only if the ionic product just exceeds the solubility product

$$K_{\mathrm{sp}} = [\mathrm{Ag^+}][\mathrm{Br^-}]$$

Therefore, $$[\mathrm{Br^-}] = \frac{K_{\mathrm{sp}}}{[\mathrm{Ag^+}]} = \frac{5\times10^{-13}}{0.05} = 10^{-11}\ \mathrm{M}$$

Also,

$$\text{Molarity} = \frac{\text{Number of moles}}{\text{Liter of solution}}$$

or $$10^{-11}\ \mathrm{mol\ L^{-1}} = \frac{\text{Number of moles}}{1\ \mathrm{L}}$$

or $$\text{Number of moles} = 10^{-11}\ \mathrm{mol}$$

Now, number of moles of KBr to be added = Given mass/Molar mass. Therefore,

Weight of KBr to be added
$$= \text{Number of moles} \times \text{Molar mass}$$
$$= 10^{-11} \times 120 = 1.2 \times 10^{-9}\ \mathrm{g}$$

33. At 25°C, the solubility product of Mg $(\mathrm{OH})_2$ is 1.0×10^{-11}. At which pH will $\mathrm{Mg^{2+}}$ ions start precipitating in the form of $\mathrm{Mg(OH)_2}$ from a solution of 0.001 M $\mathrm{Mg^{2+}}$ ions? **(AIEEE 2010)**

(A) 8 (B) 9
(C) 10 (D) 11

Solution

(C) The reaction is $\mathrm{Mg^{2+} + 2OH^- \rightleftharpoons Mg(OH)_2}$. The solubility product is

$$K_{\mathrm{sp}} = [\mathrm{Mg^{2+}}][\mathrm{OH^-}]_2$$

Therefore, $$[\mathrm{OH^-}] = \left(\frac{K_{\mathrm{sp}}}{[\mathrm{Mg^{2+}}]}\right)^{1/2} = \left(\frac{1\times10^{-11}}{10^{-3}}\right)^{1/2} = 10^{-4}\ \mathrm{M}$$

Therefore, pOH = $-\log[\mathrm{OH^-}]$ = 4. Now, since pH + pOH = 14, we get pH = 10.

34. The pH of a 0.1 M solution of the acid HQ is 3. The value of the ionization constant, K_a of this acid is **(AIEEE 2012)**

(A) 3×10^{-1} (B) 1×10^{-3}
(C) 1×10^{-5} (D) 1×10^{-7}

Solution

(C) Consider the dissociation of acid HQ

$$\mathrm{HQ \rightleftharpoons H^+ + Q^-}$$

The acid dissociation constant is

$$K_\mathrm{a} = \frac{[\mathrm{H^+}][\mathrm{Q^-}]}{[\mathrm{HQ}]} = \frac{[\mathrm{H^+}]^2}{[\mathrm{HQ}]}$$

as at equilibrium $[\mathrm{H^+}] = [\mathrm{Q^-}]$.

or $$K_\mathrm{a} = \frac{[\mathrm{H^+}]^2}{C} \Rightarrow K_\mathrm{a} \cdot C = [\mathrm{H^+}]^2$$

Given that pH = 3, this means $-\log[\mathrm{H^+}] = 3$ or $[\mathrm{H^+}] = 10^{-3}$ M. Substituting, we get

$$K_\mathrm{a} = \frac{(10^{-3})^2}{10^{-1}} = 10^{-5}$$

35. How many litters of water must be added to 1 liter of an aqueous solution of HCl with a pH of 1 to create an aqueous solution with pH of 2? **(JEE Main 2013)**

(A) 0.9 L (B) 2.0 L
(C) 9.0 L (D) 0.1 L

Solution

(C) Initial pH = 1 ⇒ $[\mathrm{H^+}] = 10^{-1} = 0.1$ M.
New pH =2 ⇒ $[\mathrm{H^+}] = 10^{-2} = 0.01$ M.
In case of dilution, $M_1V_1 = M_2V_2$

$$0.1 \times 1 = 0.01 \times V_2 \Rightarrow V_2 = 10\ \mathrm{L}$$

Volume of water added = 9.0 L

REVIEW QUESTIONS

1. Astatine, atomic number 85, is radioactive and does not occur in appreciable amounts in nature. On the basis of what you have learned in this chapter, answer the following.
(a) How would the acidity of HAt compare to HI?
(b) How would the acidity of $\mathrm{HAtO_3}$ compare with $\mathrm{HBrO_3}$?

2. $\mathrm{HClO_4}$ is a stronger proton donor than $\mathrm{HNO_3}$, but in water both acids appear to be of equal strength; they are both 100% ionized. Why is this so? What solvent property would be necessary in order to distinguish between the acidities of these two Brønsted acids?

3. Explain why the oxide ion, $\mathrm{O^{2-}}$, can function as a Lewis base but not as a Lewis acid.

4. In the reaction of calcium with oxygen to form calcium oxide, each calcium gives a pair of electrons to an oxygen atom. Why isn't this viewed as a Lewis acid–base reaction?

5. Explain why
(a) If the oxide of an element dissolves in water to give an acidic solution, the element is more likely to be a non-metal?
(b) Many chromium salts crystallize as hydrates containing the ion $\mathrm{Cr(H_2O)_6^{3+}}$. Solutions of these salts tend to be acidic.
(c) $\mathrm{Fe^{3+}}$ is expected to give the more acidic solution than $\mathrm{Fe^{2+}}$.
(d) Ions of the alkali metals have little effect on the acidity of a solution.

6. How are acidic, basic, and neutral solutions in water defined **(a)** in terms of $[H^+]$ and $[OH^-]$ and **(b)** in terms of pH?

7. Explain how acids and bases suppress the ionization of water, often called the common ion effect.

8. Explain the leveling effect of water.

9. Identify the conjugate acid–base pairs in the following reactions.

(a) $HNO_3 + N_2H_4 \rightleftharpoons NO_3^- + N_2H_5^+$

(b) $NH_3 + N_2H_5^+ \rightleftharpoons NH_4^+ + N_2H_4$

(c) $H_2PO_4^- + CO_3^{2-} \rightleftharpoons HPO_4^{2-} + HCO_3^-$

(d) $HIO_3 + HC_2O_4^- \rightleftharpoons IO_3^- + H_2C_2O_4$

10. Use Lewis structures to diagram the reaction

$$CO_2 + H_2O \rightarrow H_2CO_3$$

Identify the Lewis acid and Lewis base in this reaction.

11. (a) Hydrazine, N_2H_4, is a weaker Brønsted base than ammonia. In the following reaction, would the position of equilibrium lie to the left or to the right? Justify your answer.

$$N_2H_5^+ + NH_3 \rightleftharpoons N_2H_4 + NH_4^+$$

(b) Identify the two Brønsted acids and two Brønsted bases in the reaction

$$NH_2OH + CH_3NH_3^+ \rightleftharpoons NH_3OH^+ + CH_3NH_2$$

12. Write the chemical equation for the ionization of each of the following weak bases in water. For each of the bases, write the appropriate K_b expression

(a) $(CH_3)_3N$
(b) AsO_4^{3-}
(c) NO_2^-
(d) $(CH_3)_2N_2H_2$

13. What criterion do we use to determine whether or not the equilibrium concentration of an acid or base will be effectively the same as its initial concentration when we calculate the pH of the solution?

14. A solution of hydrazinium acetate is slightly acidic. Without looking at the tables of equilibrium constants, is K_a for acetic acid larger or smaller than K_b for hydrazine? Justify your answer.

15. Write ionic equations that illustrate how each pair of compounds can serve as a buffer pair.

(a) H_2CO_3 and $NaHCO_3$ (the "carbonate" buffer in blood)
(b) NaH_2PO_4 and Na_2HPO_4 (the "phosphate" buffer inside body cells)
(c) NH_4Cl and NH_3

16. Citric acid, found in citrus fruits, is a triprotic acid, $H_3C_6H_5O_7$. Write chemical equations for the three-step ionization of this acid in water and the corresponding K_a expressions.

17. What simplifying assumptions do we usually make in working problems involving the ionization of polyprotic acids? Why are they usually valid? Under what conditions do they fail?

18. (a) When a formic acid solution is titrated with sodium hydroxide, will the solution be acidic, neutral, or basic at the equivalence point?

(b) When a solution of hydrazine is titrated by hydrochloric acid, will the solution be acidic, neutral, or basic at the equivalence point?

(c) If you use methyl orange in the titration of CH_3COOH with NaOH, will the end point of the titration correspond to the equivalence point? Justify your answer.

19. The conjugate acid of a molecular base has the hypothetical formula, BH^+, which has a pK_a of 5.00. A solution of a salt of this cation, BHY, tests slightly basic. Will the conjugate acid of Y^-, HY, have a pK_a greater than 5.00 or less than 5.00? Explain.

20. Suppose a solution contains 0.0050 M Co^{2+} and is saturated with H_2S (with $[H_2S] = 0.1$ M). Would CoS precipitate if the solution has a pH of 3.5? (Hint: What relationship do we use to determine whether a precipitate is going to form in a solution?)

21. Use Le Chatelier's principle to explain how adjusting the pH enables the control of the concentration of $C_2O_4^{2-}$ in a solution of oxalic acid, $H_2C_2O_4$.

22. A solution of $MgBr_2$ can be changed to a solution of $MgCl_2$ by adding AgCl(s) and stirring the mixture well. In terms of the equilibria involved, explain how this happens.

23. Using Le Chatelier's principle, explain how the addition of aqueous ammonia dissolves silver chloride. If HNO_3 is added after the AgCl has dissolved in the NH_3 solution, it causes AgCl to re-precipitate. Explain why.

24. For $PbCl_3^-$, $K_{form} = 2.5 \times 10^1$. If a solution containing this complex ion is diluted with water, $PbCl_2$ precipitates. Write the equations for the equilibria involved and use them together with Le Chatelier's principle to explain how this happens.

25. Explain the buffering action in swimming pools.

26. Acetic acid, CH_3COOH, and sodium acetate, CH_3COONa (this provides the acetate ion, CH_3COO^-), can be used to make an "acetate" buffer. Does the acetate ion or the acetic acid concentration increase when a strong acid is added to the buffer? Is it the acetate ion or acetic acid that decreases when a strong base is added to the buffer? Explain your answers.

NUMERICAL PROBLEMS

1. A soft drink was put on the market with $[H^+] = 1.4 \times 10^{-5}$ mol L^{-1}. What is its pH?

2. The interaction of water droplets in rain with carbon dioxide that is naturally present in the atmosphere causes rainwater to be slightly acidic because CO_2 is an acidic anhydride. As a result, pure clean rain has a pH of about 5.7. What are the hydrogen ion and hydroxide ion concentrations in this rainwater?

3. A solution was made by dissolving 0.837 g $Ba(OH)_2$ in 100 mL final volume. What is the molar concentration of OH^- in the solution? What are the pOH and the pH? What is the hydrogen ion concentration in the solution?

4. A solution of HCl has a pH of 2.50. How many grams of HCl are there in 250 mL of this solution? How many grams of HCl are in 250 mL of an HCl solution that has twice the pH?

5. How many milliliters of 0.0100 M KOH are needed to completely neutralize the HCl in 300 mL of a hydrochloric acid solution that has a pH of 2.25?

6. Suppose 38.0 mL of 0.000200 M HCl is added to 40.0 mL of 0.000180 M NaOH. What will be the pH of the final mixture?

7. What is the pH of a 3.0×10^{-7} M solution of HCl?

8. How many milliliters of 0.10 M NaOH must be added to 200 mL of 0.010 M HCl to give a mixture with a pH of 3.00?

9. Milk of magnesia is a suspension of magnesium hydroxide in water. Although $Mg(OH)_2$ is relatively insoluble, a small amount does dissolve in the water, which makes the mixture slightly basic and gives it a pH of 10.08. How many grams of $Mg(OH)_2$ are actually dissolved in 100 mL of milk of magnesia?

10. A 1.0 M solution of acetic acid has a pH of 2.37. What percentage of the acetic acid is ionized in the solution?

11. A 0.20 M solution of a weak acid, H*A*, has a pH of 3.22. What is the percentage ionization of the acid? What is the value of K_a for the acid?

12. Periodic acid, HIO_4, is an important oxidizing agent and a moderately strong acid. In a 0.10 M solution, $[H^+] = 3.8 \times 10^{-2}$ mol L^{-1}. Calculate the K_a and pK_a for periodic acid.

13. How many moles of NH_3 must be dissolved in water to give 500 mL of solution with a pH of 11.22?

14. Barbituric acid, $HC_4H_3N_2O_3$ (abbreviated as H-*Bar*), is the parent compound of widely used sleeping drugs, the barbiturates. Its pK_a is 4.01. What is the $[H^+]$ and pH of a 0.020 M solution of H-*Bar*?

15. Calculate the pH of 0.40 M KNO_2. What is the concentration of HNO_2 in the solution?

16. A weak base *B* forms the salt *B*HCl, composed of the ions BH^+ and Cl^-. A 0.15 M solution of the salt has a pH of 4.28. What is the value of K_b for the base *B*?

17. A student added 100 mL of 0.10 M NaOH to 250 mL of a buffer that contained 0.15 M CH_3COOH and 0.25 M CH_3COO^-. By how much did the concentrations of CH_3COOH and CH_3COO^- change after the addition of the strong base?

18. **(a)** What is the pH of a solution that contains 0.15 M CH_3COOH and 0.25 M CH_3COO^-? Use $K_a = 1.8 \times 10^{-5}$ for CH_3COOH.

(b) By how much will the pH change if 25.0 mL of 0.20 M NaOH is added to 500 mL of the buffer in the above case?

19. How many grams of sodium formate, $NaCHO_2$, would have to be dissolved in 1.0 L of 0.12 M formic acid (pK_a 3.74) to make the solution a buffer for pH 3.50?

20. How many milliliters of 0.15 M HCl would have to be added to the original 100 mL of the buffer described in Problem 19 to make the pH decrease by 0.05 pH unit? How many milliliters of the same HCl solution would, if added to 100 mL of pure water, make the pH decrease by 0.05 pH unit?

21. A solution contains calcium nitrate and nickel nitrate, each at a concentration of 0.10 M. Carbon dioxide is to be bubbled in to make its concentration equal 0.030 M. What pH range would make it possible for the carbonate of one cation to precipitate but not that of the other?

22. Gold(III) chloride has $K_{sp} = 3.2 \times 10^{-25}$. Calculate the molar solubility of gold(III) chloride in **(a)** pure water, **(b)** 0.010 M HCl solution, **(c)** 0.010 M $MgCl_2$ solution and **(d)** 0.010 M $Au(NO_3)_3$ solution.

$AuCl_3(s) \rightleftharpoons Au^{3+} + 3Cl^- \qquad K_{sp} = [Au^{3+}][Cl^-]^3 = 3.2 \times 10^{-25}$

23. In an experiment 2.20 g of NaOH(*s*) is added to 250 mL of 0.10 M $FeCl_2$ solution. What mass of $Fe(OH)_2$ will be formed? What will the molar concentration of Fe^{2+} be in the final solution?

24. Suppose 50.0 mL each of 0.0100 M solutions of NaBr and $Pb(NO_3)_2$ are poured together. Does a precipitate form? If so, calculate the molar concentrations of the ions at equilibrium.

25. Calculate the pH at equivalence point when a solution of 0.10 M acetic acid is titrated with a solution of 0.10 M NaOH solution. (Given that K_a for acetic acid $= 1.9 \times 10^{-5}$.)

ADDITIONAL OBJECTIVE QUESTIONS

Single Correct Choice Type

1. In the hydrolytic equilibrium $A^- + H_2O \rightleftharpoons HA + OH^-$, $K_a = 1.0 \times 10^{-5}$ the degree of hydrolysis of 0.001 M solution of the salt is

(A) 10^{-3} (B) 10^{-4}
(C) 10^{-5} (D) 10^{-6}.

2. If *S* is the solubility of a sparingly soluble salt M_2X_3, its solubility product is equal to

(A) $9S^4$ (B) $27S^3$
(C) $6S^2$ (D) $108S^5$

3. Lewis base among the following can be

(A) NO_2 (B) SiO_2
(C) GeO_2 (D) None of these

4. Which of the following is the strongest acid ?

(A) $HClO_4$ dissolved in glacial CH_3COOH
(B) $HClO_4$ dissolved in H_2O
(C) H_2SO_4 dissolved in H_2O
(D) Glacial CH_3COOH dissolved in H_2O.

5. Neutralization reaction according to Lewis concept is a formation of

(A) salt and water. (B) acid–base adduct.
(C) coordinate compound. (D) zwitter ion.

6. Liquid ammonia ionizes to a slight extent. At –50°C, its ionic product is $K_{NH_3} = [NH_4^+][NH_2^-] = 10^{-30}$. How many amide ions, NH_2^- are present per mm^3 of pure liquid ammonia?
(A) 6.023×10^{23}
(B) 6.023×10^{14}
(C) 6.023×10^{15}
(D) 6.023×10^{-15}.

7. The degree of dissociation of pure water at 25°C is found to be 1.8×10^{-9}. Find K_w and K_d at 25°C.
(A) $3.24 \times 10^{-18}; 5.83 \times 10^{-20}$
(B) $1 \times 10^{-14}; 1.8 \times 10^{-16}$
(C) $1.8 \times 10^{-16}; 1 \times 10^{-14}$
(D) $1 \times 10^{-14}; 1 \times 10^{-14}$

8. How much water must be added to 300 mL of 0.2 M solution of CH_3COOH for the degree of dissociation of the acid to double? K_a for the acetic acid = 1.8×10^{-5}.
(A) 900 mL
(B) 1000 mL
(C) 500 mL
(D) 300 mL

9. To a 100 mL solution of 0.1 M CH_3COONa and 0.1 M CH_3COOH, 0.4 g of solid NaOH was added. Assuming volume remains constant, calculate the change in pH value? Given that pK_a (CH_3COOH) = 4.74.
(A) 0.125
(B) 0.225
(C) 0.01
(D) 0.872

10. In the hydrolytic equilibrium $B^+ + H_2O \rightleftharpoons BOH + H^+$, $K_b = 1 \times 10^{-5}$. The hydrolysis constant is:
(A) 10^{-5}
(B) 10^{-19}
(C) 10^{-10}
(D) 10^{-9}

11. The solubility product of $BaSO_4$ is 1.5×10^{-9}. The precipitation in a 0.01 M Ba^{2+} ions solution will start on adding H_2SO_4 of concentration:
(A) 10^{-9} M
(B) 10^{-8} M
(C) 10^{-7} M
(D) 10^{-6} M

12. Let the solubilities of AgC1 in H_2O, 0.01 M $CaCl_2$; 0.01 M NaCl and 0.05 M $AgNO_3$ be S_1 S_2, S_3, S_4 respectively. What is the correct relationship between these quantities?
(A) $S_1 > S_2 > S_3 > S_4$
(B) $S_1 > S_2 = S_3 > S_4$
(C) $S_3 > S_2 > S_4 > S_1$
(D) $S_4 > S_2 > S_3 > S_1$

13. pH of a mixture of HA and A^- buffer is 5. K_b of $A^- = 10^{-10}$. Hence $[HA]/[A^-]$ will be:
(A) 1
(B) 10
(C) 0.1
(B) 100

14. Calculate the $[H_3O^+]$ of blood, the pH of which is 7.3 (slightly basic)
(A) 5×10^{-8} M
(B) 6×10^{-8} M
(C) 5×10^{-9} M
(D) 4×10^{-7} M

15. How many grams of CaC_2O_4 will dissolve in one liter of saturated solution? K_{sp} of CaC_2O_4 is 2.5×10^{-9} mol^{-2} and its molecular weight is 128.
(A) 0.0064 g
(B) 0.0128 g
(C) 0.0032 g
(D) 0.0640 g

16. A solution of HC1 is diluted so that its pH changes by 0.3. How does concentration of H^+ ion change?
(A) 0.5 times of initial value
(B) 0.3 times of initial value
(C) 10^{-3} times increases
(D) None of these

17. The pH of a 0.01 M solution of acetic acid is
(A) 2.
(B) less than 2.
(C) greater than 2.
(D) cannot be predicted.

18. One drop of which of the following solution will give pink color with potassium hydroxide solution?
(A) Methyl orange
(B) Methyl red
(C) Bromothymol blue
(D) Phenolphthalein

19. The pH of 0.1 M solution of the following salts increases in the order of **(IIT-JEE 1999)**
(A) NaCl < NH_4Cl < NaCN < HCl
(B) HCl < NH_4Cl < NaCl < NaCN
(C) NaCN < NH_4Cl < NaCl < HCl
(D) HC < NaCl < NaCN < NH_4Cl

20. Arrhenius theory of acid–base is not applicable in
(A) aqueous solution.
(B) presence of water.
(C) non-aqueous solutions.
(D) none of these.

21. Which of the following is not Brönsted acid?
(A) NH_4^+
(B) HPO_4^{2-}
(C) $AlCl_3$
(D) CH_3COOH

22. Which of the following is not the characteristics of an acid?
(A) Turns blue litmus to red.
(B) Turns phenolpthalein pink from colorless.
(C) Decomposes carbonates.
(D) Forms oxy compounds of non-metals.

23. The compound which is not a Lewis acid is
(A) BF_3
(B) $AlCl_3$
(C) $SnCl_4$
(D) $BeCl_2$

24. The pH of 0.1 M CH_3COOH is 2.873. What is pH of 0.1 M NH_4OH? [$K_a(CH_3COOH) = 1.8 \times 10^{-5}$ and $K_b(NH_4OH) = 1.8 \times 10^{-5}$]
(A) 11.127
(B) 2.873
(C) 7
(D) 9.53

25. If the K_b value in the hydrolysis reaction, $B + H_2O \rightleftharpoons BOH + H^+$; is 1.0×10^{-6}, then the hydrolysis constant of the salt would be
(A) 1.0×10^{-6}
(B) 1.0×10^{-7}
(C) 1×10^{-8}
(D) 1.0×10^{-9}

26. The solubility products of $Al(OH)_3$ and $Zn(OH)_2$ are 8.5×10^{-23} and 1.8×10^{-14}, respectively. If NH_4OH is added to a solution containing Al^{3+} and Zn^{2+} ions, then substance precipitated first is
(A) $Al(OH)_3$
(B) $Zn(OH)_2$
(C) both A and B
(D) none of these.

27. The solubility product of AgCl in water at 25°C is 1.6×10^{-10}. Its solubility in the presence of 0.1 M HCl is
(A) 1.26×10^{-5}
(B) 2.52×10^{-7}
(C) 1.6×10^{-9}
(D) 1.6×10^{-8}

28. Strength of an acid can be explained on the basis of
(A) its concentration in solution.
(B) its degree of ionization.
(C) both A and B are required.
(D) It is an inherent property of acid.

29. Which of the following indicates the correct order of acidic strength of the following acids?
(I) HCOOH ($K_a = 1.8 \times 10^{-4}$)
(II) CH_3COOH ($K_a = 1.8 \times 10^{-5}$)
(III) HCN ($K_a = 4.8 \times 10^{-10}$)
(IV) HS^- ($K_a = 1 \times 10^{-14}$)

(A) I > II > III > IV (B) IV > III > II > I
(C) I > III > II > IV (D) II > UK KIV

30. In a saturated solution of silver chromate in pure water at 25°C, the concentration of chromate ion is 2×10^{-4} mol L^{-1}. The solubility product of silver chromate is
(A) 2×10^{-8} (B) 4×10^{-8}
(C) 3.2×10^{-12} (D) 3.2×10^{-11}

31. Calculate the pOH and pH of a 0.1 M CH_3COOH solution ($K_a = 1.8 \times 10^{-5}$). There is 7.5×10^{-3} % yield of OH^- ions in the given reaction $CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$
(A) 6.12, 7.88 (B) 4.12, 9.88
(C) 5.13, 8.87 (D) None of these

32. pH of 0.01 M HS^- will be
(A) $pH = 7 + \frac{pK_a}{2} + \frac{\log C}{2}$ (B) $pH = 7 - \frac{pK_a}{2} + \frac{\log C}{2}$
(C) $pH = \frac{pK_1 + pK_2}{2}$ (D) $pH = 7 + \left(\frac{pK_a + pK_b}{2}\right)$

33. A sample of 100 mL of 0.10 M acid HA ($K_a = 1 \times 10^{-5}$) is titrated with standard 0.10 M KOH. How many mL of KOH will have to be added when the pH in the titration flask will be 5.00?
(A) 0 (B) 10
(C) 100 (D) 50

34. 1.458 g of Mg reacts with 80.0 mL of HCl solution whose pH is –0.477. The change in pH after all Mg has reacted is (Assume constant volume. Mg = 24.3 g mol^{-1} and log 3 = 0.477.)
(A) –0.176 (B) + 0.477
(C) –0.2385 (D) 0.3

35. 0.1 mol of CH_3NH_3($K_b = 5 \times 10^{-4}$) is mixed with 0.08 mol of HCI and diluted to 1 L. What will be the H^+ ion concentration in the solution?
(A) 8×10^{-2} M (B) 8×10^{-11} M
(C) 1.6×10^{-11} M (D) 8×10^{-5} M

36. A buffer solution contains 100 mL of 0.01 M CH_3COOH and 200 mL of 0.02 M CH_3COONa 700 mL of water is added. The values of pH before and after dilution are ($pK_a = 4.74$)
(A) 5.04, 5.04 (B) 5.04, 0.504
(C) 5.04, 1.54 (D) 5.34, 5.34

37. A solution contains 0.1 M H_2S and 0.3 M HCl. Calculate the conc. of S^{2-} and HS^- ions in solution. Given K_{a1} and K_{a2} for H_2S are 10^{-7} and 1.3×10^{-13}, respectively.
(A) $1.44 \times 10^{-19}, 3.3 \times 10^{-7}$ (B) $1.44 \times 10^{-20}, 3.3 \times 10^{-8}$
(C) $1.44 \times 10^{-22}, 3.3 \times 10^{-3}$ (D) $1.44 \times 10^{-18}, 3.3 \times 10^{-5}$

38. To a 100 mL solution of 0.1 M CH_3COONa and 0.1 M CH_3COOH, 0.4 g of solid NaOH was added. Assuming volume remains constant, the change in pH value will be (pK_a of CH_3COOH = 4.74)
(A) 0.125 (B) 0.225
(C) 0.01 (D) 0.0872

39. What is the pH of the solution when 0.2 mol of hydrochloric acid is added to 1 L of a solution containing **(a)** 1 M each of acetic acid and acetate ion and **(b)** 0.1 M each of acetic acid and acetate ion? Assume that the total volume is 1 L. K_a for acetic acid = 1.8×10^{-5}.
(A) 4.57, 2 (B) 4.57, 1
(C) 5.57, 1 (D) 5.57, 2

40. Two buffers, (X) and (Y) of pH 4.0 and 6.0, respectively, are prepared from acid HA and the salt NaA. Both the buffers are 0.50 M in HA. What would be the pH of the solution obtained by mixing equal volumes of the two buffers? ($K_{HA} = 1.0 \times 10^{-5}$).
(A) 4.7033 (B) 5.7033
(C) 6.7033 (D) 8.7033

41. To what volume must one liter of 1 M CH_3COOH solution be diluted so that the pH of resulting solution becomes twice the original value. [Given: $K_a = 1.8 \times 10^{-5}$]
(A) 2.78×10^5 (B) 2.78×10^4
(C) 2.78×10^3 (D) 2.78×10^2

42. An acid–base indicator has K_a of 3×10^{-5}. The acid form of the indicator is red and the basic form is blue. By how much must the pH change in order to change the indicator from 75% red to 75% blue?
(A) 1.95 (B) 2.95
(C) 0.95 (D) 3.95

43. The indicator used for the titration of a weak base and strong acid is
(A) methyl orange. (B) phenophthalein.
(C) phenol red. (D) litmus paper.

44. Ammonium ion is a
(A) Lewis acid. (B) Lewis base.
(C) Brönsted acid. (D) Brönsted base.

45. When a 0.1 N solution of an acid at 25°C has a degree of ionization of 8%, the concentration of OH^- present is
(A) 1.25×10^{-3} (B) 1.25×10^{-11}
(C) 1.25×10^{-12} (D) 1.25×10^{-13}

46. A solution has 0.05 M Mg^{2+} and 0.05 M NH_3. Calculate the concentration of NH_4Cl required to prevent the formation of $Mg(OH)_2$ in solution. $K_{sp[Mg(OH)_2]} = 9.0 \times 10^{-12}$ and ionization constant of NH_3 is 1.8×10^{-5}.
(A) 4.123 M. (B) 0.67 M.
(C) 5.267 M. (D) 0.067 M.

47. When equal volumes of the following solutions are mixed, precipitation of AgCl ($K = 1.8 \times 10^{-10}$) will occur only with
(A) 10^{-4} M (Ag^+) and 10^{-4} M (Cl^-)
(B) 10^{-5} M (Ag^+) and 10^{-5} M (Cl^-)
(C) 10^{-6} M (Ag^+) and 10^{-6} M (Cl^-)
(D) 10^{-10}M (Ag^+)and 10^{-10} M (Cl^-)

48. The correct order of increasing [H_3O^+] in the following aqueous solution is
(A) 0.001 M H_2S < 0.01 M H_2SO_4< 0.01 M NaCl < 0.01 M $NaNO_2$
(B) 0.01 M NaCl < 0.01 M $NaNO_2$ < 0.01 M H_2S < 0.01 M H_2SO_4
(C) 0.01 M $NaNO_2$ < 0.01 M NaCl < 0.01 M H_2S < 0.01M H_2SO_4
(D) 0.01 M H_2S < 0.01 M NaCl < 0.01 M $NaNO_2$ < 0.01M H_2SO_4

49. To a 50 mL of 0.1 M HCl solution, 10 mL of 0.1 M NaOH is added and the resulting solution is diluted to 100 mL. What is change in pH of the HCl solution?
(A) 4.398
(B) 0.398
(C) 0.1
(D) None of these

50. What amount of solid sodium acetate be added into 1 L of the 0.1 M CH_3COOH solution so that the resulting solution has pH almost equal to pK_a $(CH_3COOH) = 4.74$?
(A) 12 g
(B) 5 g
(C) 10 g
(D) 14.924 g

51. Which of the following sulphides has maximum solubility in water?
(A) CdS $(K_{sp} = 36 \times 10^{-30})$
(B) FeS $(K_{sp} = 11 \times 10^{-20})$
(C) HgS $(K_{sp} = 32 \times 10^{-54})$
(D) ZnS $(K_{sp} = 11 \times 10^{-22})$

52. Law of mass action can be applied to aqueous solutions of weak electrolyte since
(A) reaction is always carried out in a closed vessel.
(B) pressure, temperature of surroundings remain constant.
(C) state of equilibrium exists between the ionized and unionized molecules.
(D) nothing can be predicted.

53. Given $[Ag(NH_3)_2]^+ \rightleftharpoons Ag^+ + 2NH_3$, $K_C = 6.2 \times 10^{-8}$ and $K_{sp(AgCl)} = 1.8 \times 10^{-10}$ at 298 K. Calculate the concentration of the complex in 1.0 M aqueous ammonia.
(A) 0.539
(B) 0.239
(C) 1.539
(D) 0.812

54. pH of a buffer containing 6.0 g of CH_3COOH and 8.2 g of CH_3COONa in 1 L of water is $(pK_a = 4.5)$
(A) 7.5
(B) 4.5
(C) 5.5
(D) 6.5

55. After the dissolution of a sparingly soluble salt, if hydrolysis of any one of the ions will occur, then
(A) solubility of salt decreases.
(B) solubility of salt increases
(C) there will be no effect on solubility.
(D) cannot be predicted.

56. The compound whose 0.1 M solution basic is
(A) ammonium chloride.
(B) ammonium acetate.
(C) ammonium sulphate.
(D) sodium acetate.

57. Buffering action of a mixture of CH_3COOH and CH_3COONa is maximum when the ratio of salt to acid is equal to
(A) 1.0
(B) 100.0
(C) 10.0
(D) 0.1

58. Weak acid HX has the dissociation constant 1×10^{-5}. It forms a salt NaX on reaction with alkali. The percentage hydrolysis of 0.1 M solution of NaX is
(A) 0.0001
(B) 0.01
(C) 0.1
(D) 0.15

59. The pOH of 10^{-8} M HCl is
(A) 8.
(B) 6.
(C) between 6 and 7.
(D) between 7 and 8.

60. For preparing a buffer solution of pH = 6 by mixing sodium acetate and acetic acid, the ratio of concentration of salt and acid $(K_a = 10^{-5})$ should be
(A) 1:10
(B) 10:1
(C) 100:1
(D) 1:100

61. pH of a saturated solution of $Ba(OH)_2$ is 12. Hence, K_{sp} of $Ba(OH)_2$ is
(A) 5×10^{-7} M^3
(B) 5×10^{-4} M^2
(C) 1×10^{-6} M^3
(D) 4×10^{-6} M^3

62. An acid solution of pH = 6 is diluted thousand times. The pH of solution becomes approximately.
(A) 6.99
(B) 6
(C) 4
(D) 9

63. Calculate the pH at the equivalence point of the titration between 0.1 M CH_3COOH with 0.05 M NaOH $[K_a(CH_3COOH) = 1.8 \times 10^{-5})$.]
(A) 4.75
(B) 5.63
(C) 6.63
(D) 3.63

64. The self-ionization constant for pure formic acid, $K = [HCOOH_2^+][HCOO^-]$ has been estimated as 10^{-6} at room temperate. What percentage of formic acid molecules in pure formic acid are converted to formate ion? The density of formic acid is 1.22 g cm^{-3}.
(A) 0.0037
(B) 0.037
(C) 0.37
(D) 1.037

65. The average concentration of SO_2 in the atmosphere over a city on a certain day is 10 ppm. What is the pH when the average temperate is 298 K. Given that the solubility of SO_2 in water at 298 K is 1.3653 mol L^{-1} and the pK_a of H_2SO_3 is 1.92, the pH of rain on that day is
(A) 4.865
(B) 3.865
(C) 5.865
(D) 6.865

66. How much Ag^+ would remain is solution after mixing equal volumes of 0.080 M $AgNO_3$ and 0.08 N HOCN. Given that K_{sp} of AgOCN $= 2.3 \times 10^{-7}$ and K_a of HOCN $=$ 3.3×10^{-4}.
(A) 5×10^{-5} M
(B) 5×10^{-4} M
(C) 5×10^{-3} M
(D) 5×10^{-2} M

67. A solution of HCl is diluted so that its pH changes by 0.3. How does the concentration of H^+ ion change?
(A) 0.5 times of initial value
(B) 0.6 times of initial value
(C) 10^{-3} times increases
(D) 0.2 times of initial value

68. A weak base (BOH) with $K_b = 10^{-5}$ is titrated with a strong acid, HCl. At three-fourth of the equivalent point, pH of the solution is
(A) 5 + log3
(B) 14 – 5 5 – log3
(C) 14 – 5 + log3
(D) 9.523

69. An aqueous solution contains 10% ammonia by mass and has density of 0.99 g cm^{-3}. The pH of this solution is $[K_a$ for $= 5 \times 10^{-10}$ M].
(A) 11.033
(B) 12.033
(C) 9.033
(D) 7.2033

70. A solution of 0.010 M $CdCl_2$ containing 0.010 M NH_3. What concentration of NH_4^+ ion from NH_4Cl is necessary to prevent the precipitation of $Cd(OH)_2$? $(K_{sp} = 2 \times 10^{-14}$ and K_b for $NH_4OH = 1.8 \times 10^{-5})$
(A) 0.13 M
(B) 0.23 M
(C) 0.33 M
(D) 1.13 M

71. A weak acid HA after treatment with 12 mL of 0.1 M strong base BOH has a pH of 5. At the end point, the volume of same base required is 26.6 mL. The K_a of acid is
(A) 8.219×1^{-5} (B) 8.219×10^{-7}
(C) 8.219×10^{-6} (D) 8.219×10^{-4}

72. Nicotinic acid ($K_a = 1.4 \times 10^{-5}$) is represented by the formula HNiC. Calculate its percent dissociation in a solution which contains 0.10 mol of nicotinic acid per 2.0 L of solution.
(A) 2.67 (B) 1.87
(C) 1.67 (D) 1.37

73. The ratio of pH of a solution containing 1 mol of CH_3COONa + 1 mol of HCl per liter and of other solution containing 1 mol CH_3COONa + 1 mol of acetic acid per liter will be
(A) 1:2 (B) 2:1
(C) 1:3 (D) 3:1

74. An acid type indicator, Hln, differs in color from its conjugate base (In^-). The human eye is sensitive to color differences only when the ratio $[ln^-]/[Hln]$ is greater than 10 or smaller than 0.1. What should be the minimum change in pH of the solution to observe a complete color change? ($K_a = 1.0 \times 10^{-5}$).
(A) 3 (B) 2
(C) 1 (D) 4

75. Solid $AgNO_3$ is added to a solution which is 0.1 M in Cl^- and 0.1 M in CrO_4^{2-}. K_{sp} values for AgCl and Ag_2CrO_4 are 1.7×10^{-10} and 1.9×10^{-12}, respectively. The concentration of Cl^- when Ag_2CrO_4 starts precipitating will be
(A) 3.9×10^{-5} M (B) 2.9×10^{-5} M
(C) 3.9×10^{-3} M (D) 1.9×10^{-2} M

Multiple Correct Choice Type

1. Correct options for the following reaction is $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$
(A) $K_{a(NH_4^+)} + K_{b(NH_3)} = 10^{-14}$ (B) $K_{a(NH_4^+)} \times K_{b(NH_3)} = 1/K_w$
(C) $K_{a(NH_4^+)} \times K_{b(NH_3)} = K_w$ (D) $pK_{a(NH_4^+)} + pK_{b(NH_3)} = 14$

2. The ionization constant of acetic acid is 1.74×10^{-5}. [Given log 9.3 = 0.97]. The correct options are
(A) The degree of dissociation of acetic acid in its 0.05 M solution is 1.86×10^{-2}.
(B) The concentration of acetate ion in the solution is 9.3×10^{-4} mol L^{-1}.
(C) pH of acetate ion in the solution is 3.03.
(D) pH of acetate ion in the solution is 5.12.

3. A 1 L solution of pH = 1 diluted upto 10 times. What volume of a solution with pH = 2 is to be added in diluted solution so that pH does not change
(A) 1 L (B) 10 L
(C) 100 L (D) 25 L

4. When HCl(g) is passed through a saturated solution of common salt, pure NaCl is precipitated because
(A) HCl is highly soluble in water.
(B) The ionic product $[Na^+]$ $[Cl^-]$ exceeds its solubility product (K_{sp}).
(C) The K_{sp} of NaCl is lowered by the presence of Cl^- ions.
(D) HCl causes precipitation.

5. Identify the correct statement(s)
(A) The solubility of HCN exceeds the square root of its K_{sp}
(B) When 1 mol of HCl is reacted with 1 mol of aniline in aqueous solution, the resulting solution has a pH of 7.
(C) Titration curves for the titration of 0.1 M oxalic acid with 0.1 M NaOH and 0.2 M oxalic acid with 0.2 M NaOH both pass through the same pH at the first equivalence point.
(D) A solution prepared by dissolving 0.1 mol of H_3PO_4 in 250 mL solution will have $[H_3PO_4]$ + $[H_2PO_4^-]$ + $[HPO_4^{2-}] + [PO_4^{3-}] = 0.4$ M.

6. Which of the following is the correct expression of degree of dissociation for weak acid. (Assume α << 1).
(A) $\sqrt{\dfrac{K_a}{C}}$
(B) $\sqrt{\dfrac{K_a \times C}{K_a}}$
(C) $\sqrt{\dfrac{K_w}{K_b \text{ of conjugate base}} \times \dfrac{1}{C}}$
(D) $\sqrt{K_b \text{ of conjugate base} \times C}$

7. When weak base solution (50 mL of 0.1 N NH_4OH) is titrated with strong acid 0.1 N HCl, the pH of solution initially decreases fast and then decreases slowly till near equivalence point as shown in Fig. 10.13. Which of the following is true?

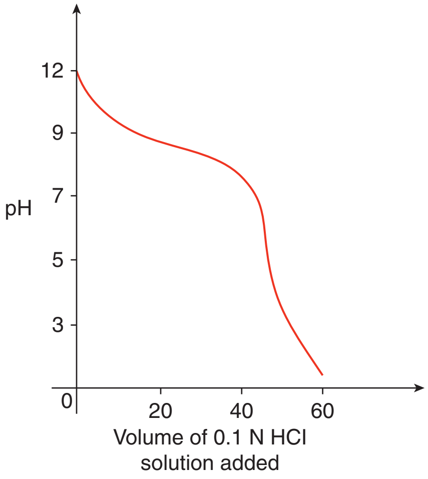


Figure 10.13

(A) The slow decrease of pH is due to the formation of an acidic buffer solution after addition of some HCl.
(B) The slope of shown pH graph will be minimum when 25 ml of 0.1 NHCl is added.
(C) The slow decrease of pH is due to formation of a basic buffer solution.
(D) The initial fast decrement in pH is due to fast consumption of free OH^- ions by HCl.

8. At what pH at 100°C, the solution will be basic (K_w at 100°C is 5.6×10^{-13})
(A) 7 (B) 6.125
(C) 6.9 (D) 7.1

9. Let the color of the indicator Hln (colorless) will be visible only when its ionized form (pink) is 25% or more in a solution. Suppose HIn ($pK_a = 9.0$) is added to a solution of pH = 9.6 predict what will happen. (Take log 2 = 0.3)
(A) Pink color will be visible.
(B) Pink color will not be visible.
(C) % of ionized form will be less than 25%.
(D) % of ionized form will be more than 25%.

10. The pH values of 0.1 M and 0.01 MNH$_4$C1 are 5.128 and 5.628, respectively. Choose the correct statement (s) from the following
(A) If dilution is the only factor, the pH should be 6.128 instead of 5.628.
(B) The given value suggests that NH_4^+ ion dissociates more in a more dilute solution.
(C) The degree of hydrolysis of NH_4^+ ion is about 1000 times less for the dilute solution.
(D) A 0.01 M solution of NH_4CI is less acidic than 0.1 M solution.

11. For K_{sp} (AgCl) = 2.8×10^{-10}. Choose the correct statements.
(A) Solubility of AgCl(s) in pure water is 1.673×10^{-5} mol L^{-1}.
(B) Solubility of AgCl(s) in a solution of 0.1 M NaCl at 25°C is 2.8×10^{-9} mol L^{-1}.
(C) Solubility of AgCl(s) in pure water is 1.256×10^{-5} mol L^{-1}.
(D) Solubility of AgCl(s) in a solution of 0.1 M NaCl at 25°C is 1.4×10^{-9} mol L^{-1}.

12. When equal volumes of the following solutions are mixed, precipitation of AgCl ($K_{sp} = 1.8 \times 10^{-10}$) will occur only with
(A) 10^{-4}M [Ag$^+$] and 10^{-4}M [HCl]
(B) 10^{-3} M [Ag$^+$] and 10^{-3}M [Cl$^-$]
(C) 10^{-6}M [Ag$^+$] and 10^{-6}M [Cl$^-$]
(B) 10^{-2} M [Ag$^+$] and 10^{-2}M [Cl$^-$]

13. Which of the following will suppress the ionization of phthalic acid in an aqueous solution?
(A) KCl (B) H_2SO
(C) HNO_3 (D) NaOH

14. Buffer solution A of a weak monoprotic acid and its sodium salt in the concentration ratio $x:y$ has pH = (pH)$_1$. Buffer solution B of the same acid and its sodium salt in the concentration ratio $y:x$ has pH = (pH)$_2$. If (pH)$_2$ − (pH)$_1$ = 1 unit and (pH)$_1$ + (pH)$_2$ = 9.5 units, then
(A) $pK_a = 4.75$ (B) $x/y = 2.36$
(C) $x/y = 3.162$ (D) $pK_a = 5.25$

Assertion–Reasoning Type

Choose the correct option from the following:
(A) Statement 1 is True, Statement 2 is True; Statement 2 is a correct explanation for Statement 1.
(B) Statement 1 is True, Statement 2 is True; Statement 2 is NOT a correct explanation for Statement 1.
(C) Statement 1 is True, Statement 2 is False.
(D) Statement 1 is False, Statement 2 is True.

1. Statement 1: If equal volumes of 0.002 M solutions of sodium iodate and copper chlorate are mixed together then copper iodate will precipitate. [K_{sp} (Cu(IO$_3$)$_2$) = 7.4×10^{-8}].

Statement 2: The ionic product in the solution relative to Cu(IO$_3$)$_2$ is less than the K_{sp} for copper iodate.

2. Statement 1: Upon dilution, degree of hydrolysis of a salt increases except in case of salt of weak acid and weak base.

Statement 2: Upon dilution, K_h of a salt increases.

3. Statement 1: Weak acid + Salt of this acid with a strong base will behave like a buffer.

Statement 2: Weak base + Salt of this base with a strong acid behave like a buffer.

4. Statement 1: Ammonium chloride is acidic in liquid ammonia solvent.

Statement 2: The strongest acid and base that can exist in self-ionizing solvent are the characteristic cation and anion, respectively.

5. Statement 1: The solubilities of AgCl in water (S_1), 0.01 M (S_2) CaCl$_2$, 0.01 M (S_3) NaCl are $S_1 > S_2 > S_3$.

Statement 2: Solubility decreases with increasing common ion concentration.

6. Statement 1: pH of buffer changes with temperature.

Statement 2: Ionic product of water (K_w) changes with temperature.

7. Statement 1: A solution of 2 : 1 molar ratio of CH_3COONa and HCl results an acidic buffer.

Statement 2: An acidic buffer is a mixture of weak acid and its salt with strong base.

8. Statement 1: The addition of silver ions to a mixture of aqueous sodium chloride and sodium bromide solution, will first precipitate AgBr rather than AgCl.

Statement 2: The value of K_{sp} of AgCl < K_{sp} of AgBr.

Comprehension Type

Read the paragraphs and answer the questions that follow.

Paragraph I

A buffer solution is resistant to change of pH on the addition of a small amount of acid or base. These solutions usually consist of a mixture of a weak acid and salt of its conjugate base, example, acidic buffers such as CH_3COOH and CH_3COONa or mixture of a weak base and salt of its conjugate acid, example, basic buffers such as NH_4OH and NH_4Cl. A salt of a weak acid and a weak base, like CH_3COONH_4 also has a buffering action. The pH of an acidic buffer and basic buffer is expressed by Henderson–Hasselbach equations as

$$pH = pK_a + \log\frac{[\text{conjugate base}]}{[\text{weak acid}]}$$

$$pOH = pK_b + \log\frac{[\text{conjugate base}]}{[\text{weak acid}]}$$

But limitation of the above equations is that these equations are applicable for buffer solutions that fit the following criteria

(a) The ratio of [conjugate base] to [weak acid] has a value between 0.1 and 10.

(b) Both [conjugate base] and [weak acid] > K_a by a factor of 100 or more.

The resistance to the change in pH on the addition of an acid or alkali is called buffer action and is measured by buffer index (B.I.)

$$\text{B.I.} = \frac{\text{Moles of base added to 1 L buffer solution}}{\text{Change in pH}}$$

B.I. is maximum when the acid and the salt are present in equal concentrations.

1. The acetate–acetic acid buffer is suitable in the pH (assume K_b of $CH_3COO^- = 10^{-9}$)
(A) –10 (B) –6
(C) –7 (D) 5.5–7.5

2. A solution of pH = 6 will be maintained by acidic buffer. Below are the few options given to a chemist. Which option will the chemist choose?
(A) K_b of $A^- = 10^{-9}$
(B) HB (0.01 M), NaB (1 M) K_b of $B^- = 10^{-10}$
(C) K_b of $X^- = 10^{-6}$
(D) Any one of these

3. pH of a mixture of 1 M benzoic acid (pK_a = 4.20) and 1 M C_6H_5COONa is 4.5. What is the volume of benzoic acid required to prepare a 300 mL buffer [log 2 = 0.3] ?
(A) 200 mL (B) 150 mL
(C) 100 mL (D) 50 mL

Paragraph II

A solution of weak acid HA was titrated with base NaOH. The equivalence point was reached when 20 mL of 0.1 M NaOH has been added. K_a of HA = 10^{-5}.

4. pH when 10 mL of 0.1 M HCl is added in the titrated solution is
(A) 3 (B) 7
(C) 5 (D) 10

5. pH of the solution obtained by mixing 10 mL 0.2 M NaOH and 10 mL of 0.2 M HA is
(A) 7 (B) 9
(C) 11 (D) 5

6. 18.25 g of HCl, 41 g of CH_3COONa and 30 g of CH_3COOH are mixed in a container and volume is made upto 10 L. Final pH of solution is [K_a of CH_3COOH at 25°C = 1.8×10^{-5}]
(A) 2.37 (B) 1.3
(C) 0.3 (D) 2.87

Paragraph III

K_{sp} of CdS = 8×10^{-27}, K_{sp} of ZnS = 1×10^{-21}, K_a of $H_2S = 1 \times 10^{-21}$

7. Which metal sulphide is precipitated first when H_2S is added?
(A) ZnS (B) Cds
(C) Both at the same time (D) Both do not form ppt.

8. What [H^+] must be maintained in a saturated H.S (0.1 M) to precipitate CdS but not ZnS, if [Cd^{+2}] = [Zn^{+2}] = 0.1 M initially?
(A) > 0.1 M (B) > 0.01
(C) > 0.2 M (D) > 0.02 M

9. When ZnS starts precipitating. What is the concentration of Cd^{+2} is left?
(A) 8×10^{-7} (B) 0.1
(C) 4×10^{-10} (D) 2×10^{-9}

Paragraph IV

The degree of dissociation of weak electrolyte is inversely proportional to the square root of concentration. It is called Ostwald dilution law

$$\alpha = \sqrt{\frac{K_a}{C}}$$

As the temperature increases, the degree of dissociation will increase.

$$\frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_{a1}}{K_{a2}}} \text{ if concentration is same}$$

$$\frac{\alpha_1}{\alpha_2} = \sqrt{\frac{C_2}{C_1}} \text{ if acid is same.}$$

10. 0.01 M CH_3COOH has 4.24% degree of dissociation. The degree of dissociation of 0.1 M CH_3COOH will be
(A) 1.33% (B) 4.24%
(C) 5.24% (D) 0.33%

11. pH of 0.005 M HCOOH [$K_a = 2 \times 10^{-4}$] is equal to
(A) 3 (B) 2
(C) 4 (D) 5

12. Which of the following is the strongest acidic solution?
(A) pH = 1 (B) pH = 2
(C) pH = 3 (D) pH = 4

13. α_1 and α_2 are in ratio of 1 : 2 where $K_{a1} = 2 \times 10^{-4}$. What will be the value of K_{a2}
(A) 8×10^{-4} (B) 2×10^{-4}
(C) 4×10^{-4} (D) 1×10^{-4}

Integer Answer Type

The answer is a **non-negative integer**.

1. What will be the pH of the resulting solution obtained by mixing 10 mL of 0.1 N HCI and 990 mL solution of NaCl?

2. The pH of an aqueous solution of a sparingly soluble metal hydroxide $M(OH)_2$ with [M^{2+}] = 0.05 M and solubility product 5×10^{-16} $mol^3\ dm^{-9}$ at 298 K is __________.

3. What will be pH of 1 L of a buffer solution containing 0.01 M NH_4Cl and 0.01 M NH_4OH having $pK_b = 5$?

4. For the reaction involving oxidation of ammonia by oxygen to form nitric oxide and water vapor, the equilibrium constant has the units $(\text{bar})^n$. Then n is __________.

5. What will be pH of the solution of the salt of weak acid and weak base? ($K_b = 1 \times 10^{-6}$ and $K_a = 1 \times 10^{-4}$).

Matrix–Match Type

1. K_1 and K_2 are first and second ionzation constants of H_2CrO_4. K_3 is dissociation constant for NH_3. Match the following:

Column I	Column II
(A) 0.1 M H_2 CrO_4	(p) $pH = 7 + 1/2pK_2 - 1/2pK_3$
(B) 0.1 M $KHCrO_4$	(q) $pH = 7 + 1/2pK_2 + 1/21og\ C$
(C) 0.1 M$(NH_4)_2CrO_4$	(r) $pH = 1/2pK_1 - 1/2\ logC$
(D) 0.1 M K_2CrO_4	(s) $pH = 1/2\ (pK_1 + pK_2)$

2. Match the salt with the pH expression.

Column I	Column II
(A) Salt of strong acid and strong base	(p) $\frac{1}{2}[pK_w + pK_a - pK_b]$
(B) Salts of weak acid and strong base	(q) $\frac{1}{2}[pK_w + pK_a - \log C]$
(C) Salt of weak base and strong acid	(r) $\frac{1}{2}[pK_w - pK_b - \log C]$
(D) Salt of weak acid and weak base	(s) $\frac{1}{2}pK_w$

3. Match the substance with the degree of hydrolysis.

Column I	Column II
(A) NH_4Cl	(p) No hydrolysis
(B) NaCI	(q) $h = \sqrt{\frac{K_h}{C}}$
(C) CH_3COONa	(r) $h = \sqrt{\frac{K_w}{CK_b}}$
(D) CH_3COONH_4	(s) $h = K_h$
	(t) pH < 7 at 25°C

ANSWERS

Review Questions

2. We would need a solvent that is a weaker proton acceptor than H_2O.

3. It has a complete valence shell.

6. **(a)** Neutral solution: $[H^+] = [OH^-] = 1.0 \times 10^{-7}$ M; pH = 7.00; **(b)** Acidic solution: $[H^+] > [OH^-]$; pH < 7.00; **(c)** Basic solution: $[H^+] < [OH^-]$; pH > 7.00

11. **(a)** The equilibrium lies to the right since reactions favor the weaker acid and base. **(b)** Acids: $CH_3NH_3^+$, NH_3OH^+; bases: NH_2OH, CH_3NH_2

13. $[HA]_{initial} < 400 \times K_a$ or if the % ionization ≥ 5%

14. Larger

18. **(a)** Basic; **(b)** acidic; **(c)** No.

19. pK_a for HY is greater than 5

20. Yes.

26. Concentration of CH_3COOH will increase; concentration of the acetic acid will decrease.

Numerical Problems

1. 4.85

2. 2.0×10^{-6} M; 5.0×10^{-9} M

3. 1.02×10^{-13} M

4. 2.9×10^{-2} g; 9.1×10^{-5} g

5. 168 mL

6. 5.28

7. 6.48

8. 18 mL

9. 3.5×10^{-4} g

10. 0.43%

11. 0.30%; 1.82×10^{-6}

12. 2.3×10^{-2}; 1.6

13. 0.075 mol

14. 1.35×10^{-3}; 2.87

15. 8.37; 2.4×10^{-6} M

16. 5.6×10^{-7}

17. $\Delta[CH_3COOH] = -0.07$ M;
$\Delta[\ CH_3COO^-] = -0.04$ M

18. **(a)** 4.97 **(b)** –0.04 pH units

19. 4.7 g

20. 41 mL

21. $CaCO_3$ will precipitate and $NiCO_3$ will not precipitate if $[CO_3^{2-}] > 4.5 \times 10^{-8}$ and $[CO_3^{2-}] < 1.3 \times 10^{-6}$

22. **(a)** 3.3×10^{-7} M;
(b) 3.2×10^{-19} M;
(c) 4.0×10^{-20} M;
(d) 1.1×10^{-8} M

23. 2.2 g solid $Fe(OH)_2$;
$[Fe^{2+}] = 2.0 \times 10^{-12}$ M

24. No precipitate will form.

25. 8.71

Additional Objective Questions

Single Correct Choice Type

1. (A) **2.** (D) **3.** (D) **4.** (B) **5.** (B)
6. (B) **7.** (B) **8.** (A) **9.** (D) **10.** (B)
11. (D) **12.** (C) **13.** (C) **14.** (A) **15.** (A)
16. (A) **17.** (C) **18.** (D) **19.** (B) **20.** (C)
21. (C) **22.** (B) **23.** (D) **24.** (A) **25.** (C)
26. (A) **27.** (C) **28.** (C) **29.** (A) **30.** (D)
31. (C) **32.** (A) **33.** (D) **34.** (D) **35.** (B)
36. (D) **37.** (B) **38.** (D) **39.** (B) **40.** (B)
41. (B) **42.** (C) **43.** (A) **44.** (C) **45.** (C)
46. (D) **47.** (A) **48.** (C) **49.** (B) **50.** (D)
51. (B) **52.** (C) **53.** (A) **54.** (B) **55.** (B)
56. (D) **57.** (A) **58.** (B) **59.** (D) **60.** (B)
61. (A) **62.** (A) **63.** (A) **64.** (A) **65.** (A)
66. (C) **67.** (A) **68.** (B) **69.** (B) **70.** (A)
71. (C) **72.** (C) **73.** (A) **74.** (B) **75.** (A)

Multiple Correct Choice Type

1. (C, D) **2.** (A, B, C) **3.** (A, B, C, D) **4.** (B, D) **5.** (A, C, D)
6. (A, C) **7.** (B, C, D) **8.** (A, C, D) **9.** (B, C) **10.** (A, B)
11. (A, B) **12.** (A, B, D) **13.** (B, C) **14.** (A, C)

Assertion–Reasoning Type

1. (D) **2.** (C) **3.** (B) **4.** (A) **5.** (A)
6. (A) **7.** (A) **8.** (C)

Comprehension Type

1. (B) **2.** (A) **3.** (C) **4.** (C) **5.** (B)
6. (D) **7.** (B) **8.** (A) **9.** (A) **10.** (A)
11. (A) **12.** (A) **13.** (A)

Integer Answer Type

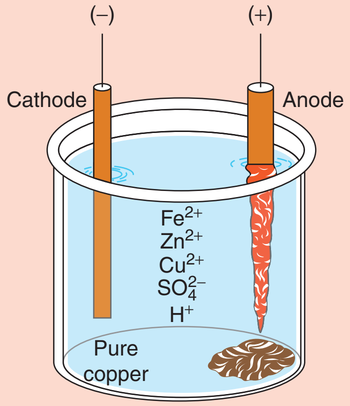
1. (3) **2.** (7) **3.** (9) **4.** (1) **5.** (6)

Matrix–Match Type

1. A → (r); B → (s); C → (p); D → (q) **2.** A → (s); B → (q); C → (r); D → (p) **3.** A → (q, r, t); B → (p); C → (q); D → (s)

11

Electrochemistry



Purification of copper

Contents

11.1 Electrochemical Cells
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11.4 Thermodynamics of a Cell
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11.6 Calculation of E°_{cell}
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Redox reactions are those in which oxidation and reduction take place simultaneously. We can use spontaneous redox reactions to produce electricity by separating the processes of oxidation (electron loss) and reduction (electron gain) and allowing them to occur in different physical locations of a system. By reversing the process, we can use electricity to make non-spontaneous redox reactions to take place for producing important products by a process called **electrolysis**. Since electricity plays a role in these systems, the processes involved are described as **electrochemical changes** and the study of these changes is called **electrochemistry**. Thus, electrochemistry is the branch of chemistry that deals with the relation between chemical changes and electricity. It deals with the study of electrical properties of electrolytes and also the chemical changes brought about by passage of electricity.

11.1 | ELECTROCHEMICAL CELLS

The devices which convert electrical energy into chemical energy or vice versa are called **electrochemical cells**. Based on the activity taking place in them, these devices are classified into two main categories: Galvanic (voltaic cells) and Electrolytic cells. The galvanic cells are further divided into chemical cells and concentration cells and are discussed first.

Galvanic Cell

A galvanic cell consists of two electrodes immersed in solutions of their respective salts known as half-cells. The two electrodes are connected externally by a metallic wire through a voltmeter and a switch, and internally by a salt bridge. When the circuit is completed by closing the switch, a redox reaction occurs in which one of the electrodes undergoes oxidation while the other undergoes reduction.

The reactions taking place in each half-cell are called half-cell reactions. Electrodes are named in accordance with the reaction occurring at them. The electrode at which reduction (or electron gain) takes place is known as the **cathode** and the electrode at which oxidation (loss of electrons) takes place is known as the **anode**.

Daniell cell is the most popular galvanic cell. It is built by two electrodes, Zn rod dipped in $ZnSO_4$ solution and Cu rod dipped in $CuSO_4$ solution, connected by a salt bridge. The redox reaction taking place in the cell is

$$\mathrm{Zn(s) + CuSO_4(aq) \rightarrow ZnSO_4(aq) + Cu(s)}$$

Zn loses two electrons and gets oxidized to Zn^{2+}, whereas copper gains two electrons and is reduced from Cu^{2+} to Cu. The overall reaction is represented in terms of two half-reactions, one representing oxidation and the other representing reduction:

$$\text{Oxidation half-reaction: } \mathrm{Zn(s) \rightarrow Zn^{2+}(aq) + 2}e^-$$

$$\text{Reduction half-reaction: } \mathrm{Cu^{2+}(aq) + 2}e^- \rightarrow \mathrm{Cu(s)}$$

$$\text{Overall redox reaction: } \mathrm{Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)}$$

This Daniell cell converts chemical energy generated by a redox reaction into electrical energy and generates an electrical potential of 1.1 V. If an increasing external opposing voltage is applied to the cell, the cell reaction continues till the voltage of 1.1 V is reached. The reaction stops thereafter and no current flows through the cell. When the externally applied voltage is increased above 1.1 V, the reaction begins to take place but in the opposite direction, that is, non-spontaneous process starts. The galvanic cell then functions like an electrolytic cell, where electrical energy is being used to carry out non-spontaneous chemical reactions (Fig. 11.1).

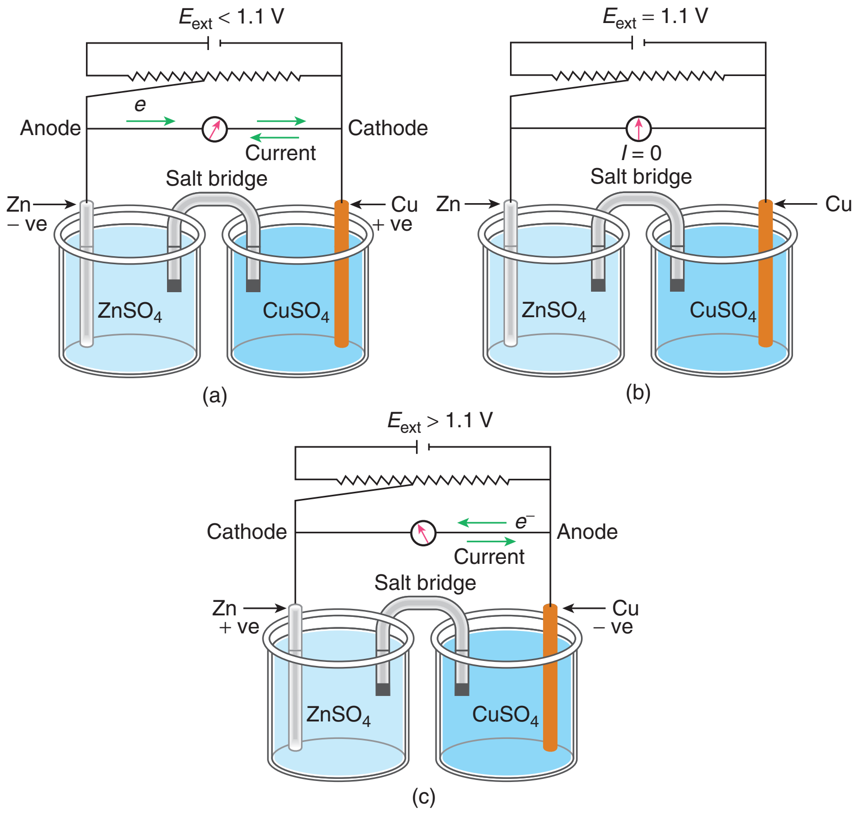


Figure 11.1 Functioning of a Daniell cell when an external voltage opposing the cell potential is applied.

A number of galvanic cells can be constructed on the pattern of Daniell cell. For example, a galvanic cell can be constructed when a silver electrode dips into a solution of $AgNO_3$ on the left and a copper electrode dips into a solution of $Cu(NO_3)_2$ on the right as illustrated in Fig. 11.2.

Some important terms related to galvanic cells are described as follows using the galvanic cell depicted in Fig 11.2.

1. **Salt bridge:** The two electrodes are connected by an external electrical circuit and the two solutions are connected by a *salt bridge*. It allows the movement of ions required to keep the solutions electrically neutral and is essential to complete the electrical circuit.
2. **Half-cell:** To produce useful *electrical* energy, the two half-reactions involved in the net reaction must be made to occur in separate containers or compartments called half-cells.
3. **Half-reaction:** When the circuit is completed by closing the switch, the reduction of Ag^+ to Ag occurs spontaneously in the half-cell on the left and oxidation of Cu to Cu^{2+} occurs spontaneously in the half-cell on the right. The reaction that takes place in each half-cell is a *half-reaction*. In the silver half-cell, the following half-reaction occurs.

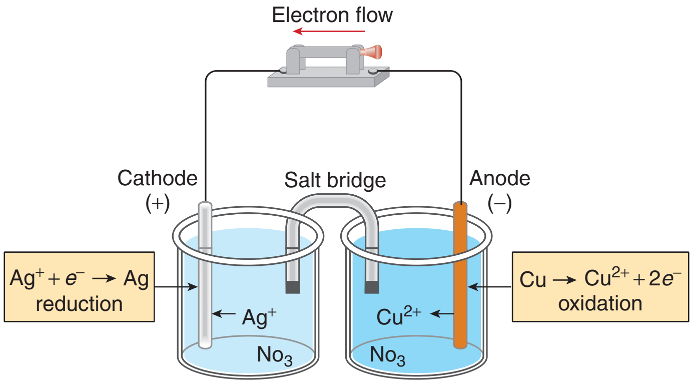


Figure 11.2 Galvanic cell.

$$Ag^+(aq) + e^- \xrightarrow{\text{Reduction}} Ag(s)$$

In the copper half-cell, the half-reaction is

$$Cu(s) \xrightarrow{\text{Oxidation}} Cu^{2+}(aq) + 2e^-$$

When these reactions take place, electrons left behind by oxidation of the copper travel through the external circuit to the other electrode where they are transferred to the silver ions, as Ag^+ is reduced to the familiar shiny silver metal.

4. **Cell reaction:** It is the overall reaction that takes place in the galvanic cell. To obtain the cell reaction, we combine the individual electrode half-reactions, making sure that the number of electrons gained in one half-reaction equals the number lost in the other. Thus, to obtain the cell reaction we multiply the half-reaction for the reduction of silver by 2 and then add the two half-reactions to obtain the net reaction. (Notice that $2e^-$ appear on each side, and so they cancel.).

$$\begin{array}{rl} 2Ag^+(aq) + 2e^- \rightarrow 2Ag(s) & \quad \text{(reduction)} \\ Cu(s) \rightarrow Cu^{2+}(aq) + 2e^- & \quad \text{(oxidation)} \\ \hline 2Ag^+(aq) + Cu(s) + \cancel{2e^-} \rightarrow 2Ag(s) + Cu^{2+}(aq) + \cancel{2e^-} & \quad \text{(cell reaction)} \end{array}$$

5. **Cathode and anode electrodes:** The **cathode** is the electrode at which reduction (electron gain) occurs. The **anode** is the electrode at which oxidation (electron loss) occurs. Thus, in the galvanic cell in Fig. 11.2, the silver electrode is the cathode and the copper electrode is the anode.
6. **Cations and anions:** In the operation of the galvanic cell, the negative ions (*anions*) move away from the cathode, where they are present in excess, and *towards the anode*, where they are needed to balance the charge of the positive ions being formed. Similarly, the positive ions (*cations*) move away from the anode, where they are in excess, and *towards the cathode*, where they can balance the charge of the anions left in excess. In fact, the reason positive ions are called cations and negative ions are called anions is because of the nature of the electrodes towards which they move.
7. **Negative polarity:** At the anode of the galvanic cell described in Fig. 11.2, copper atoms spontaneously leave the electrode and enter the solution as Cu^{2+} ions. The electrons that are left behind give the anode a slight negative charge. (We say the anode has a *negative polarity*.)
8. **Positive polarity:** At the cathode, electrons spontaneously join Ag^+ ions to produce neutral atoms, but the effect is the same as if Ag^+ ions become part of the electrode, so the cathode acquires a slight positive charge. (The cathode has a *positive polarity*.)

Role of Salt Bridge

If the electrodes in a galvanic cell are not connected internally, initially the cell generates electrical energy. The electrodes get polarized with passage of time and the cell stops working. For continuous generation of electrical energy, the electrodes need to be internally connected.

A salt bridge is usually used to connect the electrodes of a galvanic cell. It is easy to construct and consists of a gel drawn into a clean U-tube. The gel is formed by adding agar–agar into boiling water containing a suitable electrolyte like KCl. Generally, KCl is preferred because the ionic conductances of K^+ and Cl^- are almost the same. The gel holds the electrolyte in the tube as shown in Fig. 11.3.

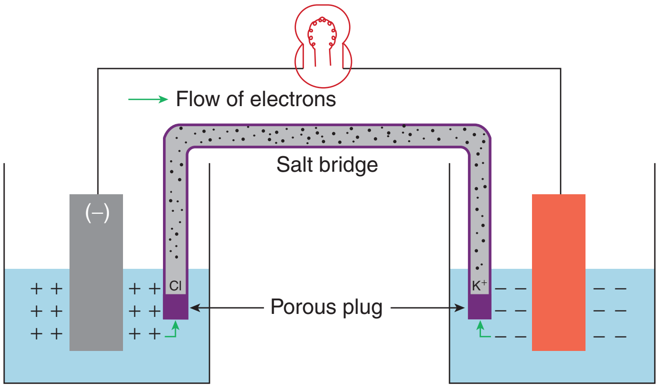


Figure 11.3 Salt bridge and electrolyte.

As the reactions proceed in the galvanic cell, there will be accumulation of particular ions around the electrodes. This results in a slowdown of the electrode reactions. From the electrolyte of the salt bridge, say KCl, the K^+ and Cl^- ions migrate towards the end of the salt bridge: K^+ ions would migrate towards the reduction electrode (cathode) while Cl^- ions would migrate towards the oxidation electrode (anode). At the oxidation electrode (anode), ions would polarize (attract) some of the oppositely charged ions towards themselves. Simultaneously, the K^+ ions would move towards the reduction electrode (cathode) and polarize the negatively charged ions surrounding the metal. Thus, the cell works as usual. Hence, a salt bridge helpful in the following ways:

1. It brings about internal contact between the electrodes.
2. It minimizes the liquid junction potential.
3. It minimizes polarization.

Liquid Junction Potential

Liquid function potential occurs when two electrolytic solutions or liquids are kept in direct contact with each other in absence of a salt bridge. The ions in two solutions will move at different speeds and thus generate a potential difference at junction of these two liquids. This is known as liquid junction potential.

Therefore,

$$E = E_{\text{oxidation}} + E_{\text{reduction}} + E_{\text{LJP}}$$

where E is the electromotive force of the cell, $E_{\text{oxidation}}$ is the oxidation half-cell, $E_{\text{reduction}}$ is the reduction half-cell and E_{LJP} is the liquid junction potential.

When salt bridge is used, it ensures that $E_{\text{LJP}} = 0$, since, the mobilities of K^+ and Cl^- are the same, (KCl is used as a paste in salt bridge) ensuring no LJP is built.

11.2 | ELECTRODE POTENTIAL

The potential difference that develops between the electrode and the electrolyte is called the **electrode potential**. The electrode potential which is determined when the concentration of all solutes is unity at standard conditions of temperature and pressure is known as **standard electrode potential**. It is useful to think of each half-cell as having a certain natural tendency to acquire electrons and proceed as a *reduction*. The magnitude of this tendency is expressed by the half-reaction's **reduction potential**. When measured under standard conditions, the reduction potential is called the **standard reduction potential**. **According to IUPAC convention, standard electrode potential is now expressed in terms of standard reduction potential**. By definition, a potential of 1 volt (V) is produced when 1 joule (J) of energy is used to transport 1 coulomb (C) of electrical charge across the potential.

$$1\ \text{V} = \frac{1\ \text{J}}{1\ \text{C}}$$

The standard state for electrochemistry is defined as a system where the temperature is 298 K, all concentrations are 1 M, and any gases are at 1.00 bar pressure.

Oxidation and Reduction Potential

If oxidation occurs at the electrode, at equilibrium the potential of the electrode can be termed as **oxidation potential**. For the zinc electrode, the reaction can be represented as

$$\mathrm{Zn(s)} \rightleftharpoons \mathrm{Zn^{2+}(aq)} + 2e^-$$

The electrode in which oxidation occurs at equilibrium is referred to as a **negative electrode**. For example, zinc electrode with 1 M $ZnSO_4$ at 298 K offers an oxidation potential of +0.76 V.

If reduction occurs at the electrode, at equilibrium the potential of the electrode is referred to as **reduction potential**. For the zinc electrode, the reaction can be represented as

$$\mathrm{Zn^{2+}(aq)} + 2e^- \rightleftharpoons \mathrm{Zn(s)}$$

If reduction occurs at equilibrium in an electrode, it is termed as **positive electrode**. The reduction potential of a zinc electrode with 1 M $ZnSO_4$ at 298 K is –0.76 V.

Note: By comparing the oxidation and reduction potential values of the same electrode, the spontaneous reaction occurring at the electrode can be predicted. In case of zinc electrode, the oxidation potential is more positive than its reduction potential. Thus, oxidation is a spontaneous reaction. However, polarity of an electrode depends on the other electrode to which it is connected.

Note: Standard reduction potential = SRP
Standard oxidation potential = SOP
For the same electrode, SRP = – SOP
Also, RP = – OP

Potential of a Cell or EMF

A current flows from one electrode to the other, indicating that the two electrodes of the cell are at different potentials. The potential difference between the two electrodes is known as the cell potential. It is the *maximum* potential that a given cell can generate and is represented by E_{cell}, and it depends on the composition of the electrodes, the concentrations of the ions in the half-cells, and the temperature. When the system is at standard state, the potential of a galvanic cell is the standard cell potential, symbolized by E°_{cell}. The potential generated by a galvanic cell, when no current is drawn through the cell, is also called the electromotive force (EMF or emf). If charge flows from a cell, some of the cell's voltage is lost overcoming its own internal resistance, and the measured voltage is less than the original E_{cell}.

When two half-cells are connected to make a galvanic cell, the one with the larger standard reduction potential (the one with the greater tendency to undergo reduction) acquires electrons from the half-cell with the lower standard reduction potential, which is therefore forced to undergo oxidation. The standard cell potential, which is always taken to be a positive number, represents the *difference* between the standard reduction potential of one half-cell and the standard reduction potential of the other. In general, therefore,

(11.1)

Knowing the single electrode potential of the two electrodes, the potential of the cell or the electromotive force of the cell formed from them can be obtained. For example, consider the cell to be constructed by coupling of an iron and a nickel electrode. If the electrode potentials of the two electrodes at 298 K are – 0.44 V and – 0.24 V in that order, the EMF of the cell can be obtained. The iron electrode (Fe^{2+}/Fe) is the oxidation electrode and nickel electrode (Ni^{2+}/Ni) is the reduction electrode.

So,

$$E_{\text{cell}} = E_{\mathrm{Ni^{2+}/Ni}} - E_{\mathrm{Fe^{2+}/Fe}} = -0.24 - (-0.44) = +0.2\ \mathrm{V}$$

The *magnitude* of the cell potential is a measure of the driving force behind a reaction. The larger the value of the cell potential, the farther is the reaction from equilibrium. The *sign* of the cell potential tells us the direction in which the reaction must shift to reach equilibrium. The fact that E° is positive for the nickel–iron cell tells us that when the system is at standard conditions, it has to shift to the right to reach equilibrium. Reactions for which E° is positive, therefore, have equilibrium constants that favor the formation of the products of the reaction. A reaction with a positive E° should occur naturally and is referred to as **spontaneous** considering concentration of all ions is unity.

Note: Though we use the terms potential difference and EMF interchangeably, there is a difference between both. While potential difference is the difference between the electrode potentials, EMF is the potential difference between the electrodes when no current is flowing. Potential difference is always less than EMF (which is the maximum voltage which can be obtained from a cell). EMF ensures steady flow of current in the circuit. Potential difference can be measured through voltmeter but EMF is measured by potentiometric methods.

Reversible and Irreversible Cells

Consider an electrochemical cell of emf E. For the cell to be termed as a **reversible cell**, the two conditions required are:

1. On application of an opposing emf exactly equal to E, the cell reaction stops.
2. On application of an emf, infinitesimally more than E, the direction of cell reaction is reversed.

For example, a Daniell cell with emf value 1.1 V is reversible if the following cell reaction stops on application of emf of –1.1 V.

$$\text{Zn(s)} + \text{Cu}^{2+}\text{(aq)} \rightarrow \text{Cu(s)} + \text{Zn}^{2+}\text{(aq)}$$

The direction of cell reaction is reversed as follows when the opposing emf is slightly more than –1.1 V.

$$\text{Cu(s)} + \text{Zn}^{2+}\text{(aq)} \rightarrow \text{Zn(s)} + \text{Cu}^{2+}\text{(aq)}$$

The electrochemical cells that do not satisfy these two conditions are said to be **irreversible cells**. For example, consider a cell consisting of zinc and silver electrodes dipped in a solution of sulphuric acid with the emf of the cell for the following cell reaction as E.

$$\text{Zn(s)} + 2\text{H}^{+}\text{(aq)} \rightarrow \text{Zn}^{2+}\text{(aq)} + \text{H}_2\text{(g)}$$

When an opposing emf is applied, the cell reaction is not reversed but takes place as follows:

$$\text{Ag(s)} + 2\text{H}^{+}\text{(aq)} \rightarrow 2\text{Ag}^{+}\text{(aq)} + \text{H}_2\text{(g)}$$

Electrochemical Conventions

There are some universal conventions and notations to be adopted in describing and representing a galvanic cell.

1. The interface across which a potential develops is denoted by either a single vertical line (|) or a semicolon (;). For example, copper electrode containing 1 M CuSO_4 is represented as:

$$\text{Cu}\,|\,\text{CuSO}_4\ (1\ \text{M}) \quad \text{or} \quad \text{Cu;CuSO}_4\ (1\ \text{M})$$

2. Representation of a cell will have the oxidation electrode (anode) on the LHS and the reduction electrode (cathode) on the RHS. The salt bridge used to connect the electrodes is represented by double vertical lines (||). For example, a galvanic cell can be represented as:

$$\text{Cu}\,|\,\text{CuSO}_4(1\ \text{M})\,\|\,\text{AgNO}_3(1\ \text{M})\,|\,\text{Ag}$$

3. The emf of a cell is represented as:

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} \tag{11.2}$$

where E_{right} and E_{left} are the standard electrode potentials (reduction electrode potentials) of RHS and LHS electrodes, respectively.

In the above galvanic cell, the half-cell reactions are:

At the cathode: $2\mathrm{Ag}^+(\mathrm{aq}) + 2e^- \rightarrow 2\mathrm{Ag}\ (\mathrm{s})$ (Reduction half-reaction)
At the anode: $\mathrm{Cu}\ (\mathrm{s}) \rightarrow \mathrm{Cu}^{2+}(\mathrm{aq}) + 2e^-$ (Oxidation half-reaction)
The emf of the cell can be represented as:

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = E_{\mathrm{Ag^+/Ag}} - E_{\mathrm{Cu^{2+}/Cu}}$$

$$\underbrace{\overbrace{\underset{\substack{\text{Oxidation}\\\text{electrode}}}{\mathrm{Cu(s)}}\,|\,\underset{\substack{\text{Anode}\\\text{electrolyte}}}{\mathrm{Cu^{2+}(aq)}}}^{\text{Anode}}}_{\text{Anode half-cell}}\quad \overset{\substack{\text{Salt}\\\text{bridge}\\\downarrow}}{||}\quad \underbrace{\overbrace{\underset{\substack{\text{Reduction}\\\text{electrolyte}}}{\mathrm{Ag^{+}(aq)}}\,|\,\underset{\substack{\text{Cathode}\\\text{electrode}}}{\mathrm{Ag(s)}}}^{\text{Cathode}}}_{\text{Cathode half-cell}}$$

Note: Always read from left to right.

Solved Example 11-1

Enter the balanced chemical equation that describes the electrochemical cell that is represented by the cell notation as shown.

$$\mathrm{Fe(s)|Fe^{3+}(aq)||Sn^{4+}(aq), Sn^{2+}(aq)|Pt(s)}$$

Solution

The reaction to the left of the double line represents the anode of the cell. At the anode an oxidation is occurring. Write the oxidation half reaction.

$$\mathrm{Fe(s)} \rightarrow \mathrm{Fe^{3+}} + 3e^-$$

The cathode is represented on the right side of the equation. Reduction occurs at the cathode. Write the half reaction for the reduction.

$$\mathrm{Sn^{4+}} + 2e^- \rightarrow \mathrm{Sn^{2+}}$$

Use the elements in the above two reactions to write an unbalanced equation.

$$\mathrm{Fe(s) + Sn^{4+}(aq) \rightarrow Fe^{3+}(aq) + Sn^{2+}(aq)}$$

Balance the equation to ensure that the charges are equal on both sides of the equation.

$$\mathrm{2Fe(s) + 3Sn^{4+}(aq) \rightarrow 2Fe^{3+}(aq) + 3Sn^{2+}(aq)}$$

Solved Example 11-2

Enter the balanced half reaction that takes place at the anode for the electrochemical cell shown. Be sure to include electrons.

$$\mathrm{Mg(s)|Mg^{2+}(aq)||Cu^{2+}(aq)|Cu(s)}$$

Solution

The reaction at the anode is always written on the left side of the (symbol. As the reaction at the anode is oxidation, Mg will lose electrons. The equation for the half reaction is,

$$\mathrm{Mg(s) \rightarrow Mg^{2+}(aq)} + 2e^-$$

Solved Example 11-3

Enter the cell notation for an electrochemical cell that has the electrode reactions shown. If needed, use platinum or graphite as an inert electrode.

(a) $Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$

$Cr(s) \rightarrow Cr^{3+}(aq) + 3e^-$

(b) $Cl_2(g) + 2e^- \rightarrow Cl^-(aq)$

$Cd(s) \rightarrow Cd^{2+}(aq) + 2e^-$

Solution

(a) In cell notation, the anode is written on the left side of the symbol (||). The reaction $Cr(s) \rightarrow Cr^{3+}(aq) + 3e^-$ is an oxidation and therefore occurs at the anode. It is therefore the anode and is an oxidation reaction.

$$Cr(s)|Cr^{3+}(aq)||Pb^{2+}(aq)|Pb(s)$$

(b) The reaction $Cl_2(g) + 2e^- \rightarrow Cl^-(aq)$ is a reduction and will be written on the right side of the symbol (||). Notice that neither of the two phases of chlorine is solid. An electrode of platinum must be provided. At the metal the Cl_2 will be able to pick up its electrons and split into $2Cl^-(aq)$ anions.

$$Cd(s)|Cd^{2+}(aq)||Cl^-(aq)|Cl_2(g)|Pt$$

Solved Example 11-4

The value for the standard emf (electromotive force) of a galvanic cell described by the balanced chemical equation is 1.03. Determine the value (V) of the standard half-cell potential for the $AuCl_4^-/Au$ couple. (Standard reduction potential $Fe^{3+} \rightarrow Fe$, –0.04 V)

$$Fe(s) + AuCl_4^-(aq) \rightarrow Fe^{3+}(aq) + Au(s) + 4Cl^-(aq)$$

Solution

The emf of the cell is equal to the standard reduction potential plus the standard oxidation potential of the two half reactions. The standard reduction potential of $Fe^{3+} \rightarrow Fe$ is –0.04 V. In the above reaction, Fe is actually being oxidized. To find the oxidation potential, reverse the sign of the reduction potential. The oxidation potential of $Fe \rightarrow Fe^{3+}$ is therefore 0.04 V. Subtract this from the emf of the cell to determine the standard half-cell potential of the $AuCl_4^-/Au$ couple.

$$E^{o}_{AuCl_4^-/Au} = 1.03 - 0.04 = 0.99\ V$$

Solved Example 11-5

The following electrochemical cell has been set up

$$Pt(1)\,|\,Fe^{3+}, Fe^{2+}(a=1)\,||\,Ce^{4+}, Ce^{3+}(a=1)\,|\,Pt(2)$$

Given that $E^{o}_{Fe^{3+}/Fe^{2+}} = 0.77\ V$, $E^{o}_{Ce^{4+}/Ce^{3+}} = 1.61\ V$. If an ammeter is connected between the two platinum electrodes, predict the direction of flow of current. Will the current increase or decrease with time?

Solution

The expression for E^{o}_{cell} is $E^{o}_{cell} = E^{o}_{cathode} - E^{o}_{anode}$

At the cathode: $Ce^{4+} + e^- \rightarrow Ce^{3+}$

At the anode: $Fe^{2+} \rightarrow Fe^{3+} + e^-$

Therefore, $E^{o}_{cell} = 1.61 - 0.77 = 0.84\ V$

As the value of E^{o}_{cell} is greater than zero, so the current will flow from right to left because left hand is anode, whereas the right one is cathode. Also, the current will decrease with time and the reaction will ultimately stop.

Solved Example 11-6

Use the standard cell potential for the following reaction

$$Cu(s) + 2H^+(aq) \rightleftharpoons Cu^{2+}(aq) + H_2(g) \quad E^{o} = -0.34\ V$$

to predict the standard cell potential for the opposite reaction

$$Cu^{2+}(aq) + H_2(g) \rightleftharpoons Cu(s) + 2H^+(aq) \quad E^{o} = ?$$

Solution

Turning the reaction around does not change the relative strengths of Cu^{2+} and H^+ ions as oxidizing agents or copper metal and H_2 as reducing agents. The *magnitude* of the potential, therefore, must remain the same. But turning the equation around changes the *sign* of the cell potential and can therefore turn an unfavorable reaction into one that is spontaneous, or vice versa. The standard cell potential for the reduction of Cu^{2+} ions by H_2 gas is therefore +0.34 V.

$$Cu^{2+}(aq) + H_2(g) \rightleftharpoons Cu(s) + 2H^+(aq)$$
$$E^\circ = -(-0.34) = +0.34\ \text{V}$$

Note that for a spontaneous redox reaction, E° of the cell should be positive. The negative value of E° tells us why copper does not displace hydrogen from dilute acids or water.

Solved Example 11-7

Calculate the minimum voltage required to bring about the electrolysis of 1 M copper sulphate solution at 25°C. Given that $E^\circ_{Cu^{2+}/Cu} = 0.34$ V and $E^\circ_{H_2O/H^+} = -1.23$ V.

Solution

Reduction half-cell reaction:

$$Cu^{2+} + 2e^- \rightarrow Cu \qquad E^\circ = 0.34\ \text{V}$$

Oxidation half-cell reaction:

$$H_2O \rightarrow 2H^+ + \tfrac{1}{2}O_2 + 2e^- \qquad E^\circ = -1.23\ \text{V}$$

Overall cell reaction:

$$Cu^{2+} + H_2O \rightarrow Cu + \tfrac{1}{2}O_2 + 2H^+$$
$$E^\circ = 0.34 + (-1.23) = -0.89\ \text{V}$$

So, the minimum voltage required to bring about electrolysis = 0.89 V.

11.3 | MEASUREMENT OF ELECTRODE POTENTIAL

The potential of an electrode cannot be accurately, directly measured. It is not feasible to connect a measuring device to the solution of electrode, as it may lead to another equilibrium along with the existing one. The problem can be overcome if the electrode is connected to another electrode of known potential. Such an electrode is termed as **reference electrode**. From the measured emf, the potential of the electrode can be obtained by subtracting the potential of the reference electrode.

Any electrode of known potential cannot be treated as a reference electrode. The criteria for an electrode to act as a reference electrode are:

1. The potential of such an electrode should be known, under the conditions of utility.
2. The potential of the electrode should show minimum variation with temperature. In other words, the potential gradient with respect to temperature should be minimum.

Some Reference Electrodes

The most commonly used reference electrode is the **hydrogen electrode**. The potential of all other electrodes are measured with respect to the hydrogen electrode. Hence, it is called a **primary reference electrode**. There are a few more reference electrodes available which are standardized using standard hydrogen electrode (SHE) and then used as reference electrodes for measuring potential of other electrodes. Such reference electrodes are termed as subsidiary or **secondary reference electrodes**. Calomel electrode and silver–silver chloride electrodes are the most popular secondary reference electrodes.

Standard Hydrogen Electrode (SHE)

A standard (normal) hydrogen electrode (SHE/NHE) consists of a platinum-foil dipped in 1.0 M HCl. The platinum foil is enclosed in a thick-walled glass tube and connected to an external contact wire. Pure hydrogen is passed into the container at 1 bar pressure through the inlet at the top and the temperature is maintained at 298 K. Excess of hydrogen leaves the electrode through the outlet at the bottom (Fig. 11.4).

Pure hydrogen gets adsorbed onto the Pt surface and is in contact with H^+ ions in the solution. It forms a reversible electrode and can be represented as:

$$\text{Pt}, \text{H}_2(1\text{ atm}) \mid (1.0\text{ M})\text{HCl}$$

If reduction occurs at the electrode, the reaction taking place will be:

$$2\text{H}^+(\text{aq}) + 2e^- \rightleftharpoons \text{H}_2(\text{g})$$

As the potential cannot be measured directly, it is conventionally assumed to be zero at 298 K. The EMF of the cell (E°_{cell}) is determined at a standard condition and since E° of SHE is assumed to be zero, the potential of the second electrode can be obtained. The electrode potential, as a practice is reported as reduction potential and is a measure of reduction potential of an electrode with respect to SHE.

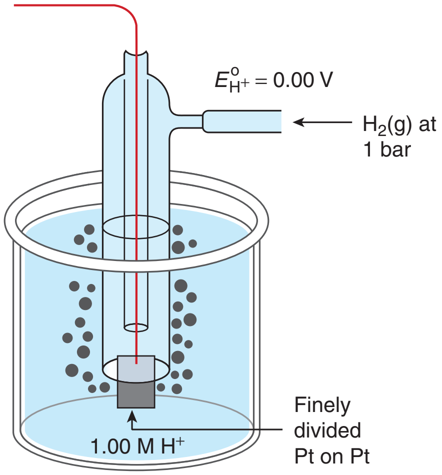


Figure 11.4 Standard hydrogen electrode.

Measurement of EMF of Galvanic Cell

Let us consider the case when the hydrogen electrode connected to a copper half-cell forms a galvanic cell. When we use a voltmeter to measure the potential of the cell (Fig. 11.5), we find that the copper electrode carries a positive charge and the hydrogen electrode a negative charge. Therefore, copper must be the cathode, and Cu^{2+} is reduced to Cu when the cell operates.

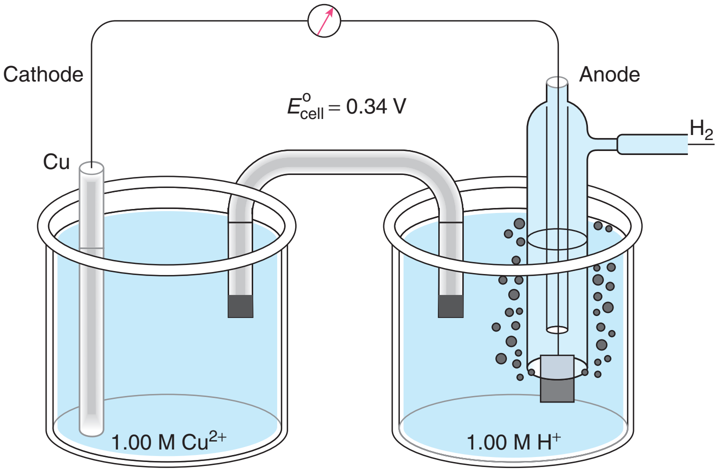


Figure 11.5 A galvanic cell composed of copper and hydrogen half-cells.

Similarly, hydrogen must be the anode, and H_2 is oxidized to H^+. The half-reactions and cell reaction, therefore, are as follows:

At the anode: $\text{H}_2(\text{g}) \rightarrow 2\text{H}^+(\text{aq}) + 2e^-$
At the cathode: $\text{Cu}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Cu}(\text{s})$
Overall cell reaction: $\text{Cu}^{2+}(\text{aq}) + \text{H}_2(\text{g}) \rightarrow \text{Cu}(\text{s}) + 2\text{H}^+(\text{aq})$

The standard potential of the cell is given by

$$E^\circ_{\text{cell}} = E^\circ_{\text{Cu}^{2+}/\text{Cu}} - E^\circ_{\text{H}^+/\frac{1}{2}\text{H}_2}$$

The measured cell potential is 0.34 V and $E^\circ_{\text{H}^+/\frac{1}{2}\text{H}_2}$ is 0.0 V. Relative to the hydrogen electrode, then, the standard reduction potential of Cu^{2+} is +0.34 V.

Note: In a galvanic cell, the measured cell potential is always taken to be positive value. Relative to the hydrogen electrode, then, the standard reduction potential of Cu^{2+} is +0.34 V. (We have written the value with a plus sign because some standard reduction potentials are negative.)

Calomel Electrode

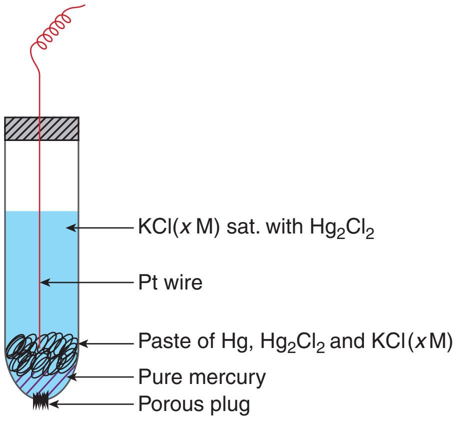

KCl(x M) sat. with Hg_2Cl_2
Pt wire
Paste of Hg, Hg_2Cl_2 and KCl(x M)
Pure mercury
Porous plug

Figure 11.6 Calomel electrode.

Calomel is the common name for mercurous chloride and it is sparingly soluble in water. The electrode consists of a thin layer of pure mercury at the bottom of the container. It is covered with a paste of Hg, Hg_2Cl_2 and KCl of known concentration. The rest of the container is filled with KCl solution of a known concentration, saturated with Hg_2Cl_2 (Fig. 11.6).

The electrode can be represented as:

$$\text{Pt, Hg(l), Hg}_2\text{Cl}_2\text{(s)}\,|\,\text{KCl}(x\text{ M}) \text{ saturated with Hg}_2\text{Cl}_2$$

It is a reversible electrode. If reduction occurs at this electrode, the reaction can be represented as:

At the anode: $$Hg_2Cl_2(s) \rightleftharpoons Hg_2^{2+}(aq) + 2Cl^-(aq)$$

At the cathode: $$Hg_2^{2+}(aq) + 2e^- \rightleftharpoons 2Hg(l)$$

Overall cell reaction: $$Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2Hg(l) + 2Cl^-(aq)$$

It is easy to construct and easy to transport. It provides almost a constant potential value with varying temperature and finds application in laboratories for measuring potential of an electrode. It is used in corrosion studies.
In case of complicated half-cell reactions like

$$\text{Pt,}\underset{\text{(liquid)}}{\text{Hg}}\text{,}\underset{\text{(solid)}}{\text{Hg}_2\text{Cl}_2}\,|\,\underset{(x\text{ M})}{\text{KCl}}\;\;\text{(saturated with Hg}_2\text{Cl}_2\text{)}$$

To write the half-cell reaction:
Step 1: Write the oxidation number of all the elements.

$$\underset{\substack{\downarrow\\0}}{\text{Pt}},\;\underset{\substack{\downarrow\\0}}{\text{Hg}},\;\underset{\substack{\downarrow\\+1}}{\text{Hg}_2}\,\underset{\substack{\downarrow\\-1}}{\text{Cl}_2}\,|\,\underset{\substack{\downarrow\\+1}}{\text{K}}\underset{\substack{\downarrow\\-1}}{\text{Cl}}$$

Step 2: Read half-cell notation from left to right and observe the change in oxidation number. In the given cell reaction, Hg is getting oxidized from 0 to +1. The fundamental oxidation reaction is:

$$Hg \rightarrow Hg_2^{2+} + 2e^-$$

Step 3: Balance and write the reaction in terms of species given in the half-cell.

$$2Hg + 2Cl^- \rightarrow Hg_2Cl_2 + 2e^-$$

Electrochemical Series

The standard reduction potentials of many half-reactions can be compared to that for the standard hydrogen electrode in the manner described above for galvanic cell. Table 11.1 lists values obtained for some typical half-reactions. They are arranged in decreasing order—the half-reactions at the top have the greatest tendency to occur as reduction, while those at the bottom have the least tendency to occur as reduction. Some important observations are:

1. Substances located to the left of the double arrows are *oxidizing agents*, because they become reduced when the reactions proceed in the forward direction. The best oxidizing agents are those most easily reduced, and they are located at the top of the table (e.g., F_2).
2. Substances located to the right of the double arrows are *reducing agents*; they become oxidized when the reactions proceed from right to left. The best reducing agents are those found at the bottom of the table (e.g., Li).

Table 11.1 Standard Reduction Potentials at 25°C

Half-Reaction	$E°$ (V)
Stronger oxidizing agent	
$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$	+2.87
$S_2O_8^{2-}(aq) + 2e^- \rightleftharpoons 2SO_4^{2-}(aq)$	+2.01
$PbO_2(s) + HSO_4^-(aq) + 3H^+(aq) + 2e^- \rightleftharpoons PbSO_4(s) + 2H_2O$	+1.69
$2HOCl(aq) + 2H^+(aq) + 2e^- \rightleftharpoons Cl_2(g) + 2H_2O$	+1.63

(*Continued*)

Table 11.1 (Continued)

Half-Reaction	*E*° (V)
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O$	+1.51
$PbO_2(s) + 4H^+(aq) + 2e^- \rightleftharpoons Pb^{2+}(aq) + 2H_2O$	+1.46
$BrO_3^-(aq) + 6H^+(aq) + 6e^- \rightleftharpoons Br^-(aq) + 3H_2O$	+1.44
$Au^{3+}(aq) + 3e^- \rightleftharpoons Au(s)$	+1.42
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$	+1.36
$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O$	+1.23
$Br_2(aq) + 2e^- \rightleftharpoons 2Br^-(aq)$	+1.07
$NO_3^-(aq) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O$	+0.96
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77
$I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)$	+0.54
$NiO_2(s) + 2H_2O + 2e^- \rightleftharpoons Ni(OH)_2(s) + 2OH^-(aq)$	+0.49
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.34
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightleftharpoons H_2SO_3(aq) + H_2O$	+0.17
$AgBr(s) + e^- \rightleftharpoons Ag(s) + Br^-(aq)$	+0.07
$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	0
$Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s)$	−0.14
$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$	−0.25
$Co^{2+}(aq) + 2e^- \rightleftharpoons Co(s)$	−0.28
$PbSO_4(s) + H^+(aq) + 2e^- \rightleftharpoons Pb(s) + HSO_4^-(aq)$	−0.36
$Cd^{2+}(aq) + 2e^- \rightleftharpoons Cd(s)$	−0.40
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	−0.44
$Cr^{3+}(aq) + 3e^- \rightleftharpoons Cr(s)$	−0.74
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	−0.76
$2H_2O + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$	−0.83
$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$	−1.66
$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$	−2.37
$Na^+(aq) + e^- \rightleftharpoons Na(s)$	−2.71
$Ca^{2+}(aq) + 2e^- \rightleftharpoons Ca(s)$	−2.76
$K^+(aq) + e^- \rightleftharpoons K(s)$	−2.92
$Li^+(aq) + e^- \rightleftharpoons Li(s)$	−3.05
Stronger reducing agent	

Applications of Electrochemical Series

The electrochemical series has several practical applications in chemistry.

1. Higher the reduction potential, greater is the tendency of the element to get reduced. Hence, the relative oxidizing and reducing abilities of the elements can be compared easily. For instance, among Zn and Cu systems, zinc system has lower reduction potential (–0.76 V) than Cu (+0.34 V). So, zinc system has more reducing ability than Cu. *Lower the reduction potential, greater is the reducing ability*.
2. A metal placed higher in the series is anodic to other metals which lie below it. An element can displace all elements that lie below it in the series, from their salt solutions. For example, zinc shavings added to a hot saturated solution of $CuSO_4$ can displace copper from the salt. In other words, displacement reactions can be predicted.
3. Knowledge of electrochemical series helps in selection of electrode assemblies, to construct the galvanic cells of the desired EMF.
4. The polarity of the electrode system and the electrode reaction can be easily predicted.
5. Spontaneity and feasibility of the cell under construction can be easily predicted.

11.4 | THERMODYNAMICS OF A CELL

Cell Potential and Gibbs Energy Change

In a galvanic cell, oxidation reaction occurs at the anode and reduction occurs at the cathode. Both the electrodes are at different potential values. The difference in potential of the electrodes is the electromotive force (emf). It is also referred to as the vigor with which the cell works and is the measure of chemical reactions occurring in the cell. In a spontaneous reaction, change in Gibbs' energy (ΔG) decreases. Larger the decrease in free energy, greater would be the emf. Mathematically, it can be expressed as:

$$\Delta G = \text{maximum useful work}, \Delta G = w_{\text{Electrical}}$$

$$\Delta G = Q_{\text{total}} \times E_{\text{cell}} \tag{11.3}$$

$$\Delta G = (-nF) \times E_{\text{cell}}$$

where n is the number of moles of electrons transferred, F is the charge of 1 mol of electrons ($1.6 \times 10^{-19} \times 6.022 \times 10^{23} \cong 96\lfloor 00$ C) and E_{cell} is the potential of the cell.
Similarly,

$$-\Delta G^{o} = nFE^{o}_{\text{cell}} \tag{11.4}$$

Thus, from the standard potential of a cell reaction, we can obtain the standard Gibbs energy of the reaction. The value of Gibb's energy can be used to calculate the equilibrium constant of the reaction. For any reaction

$$\Delta G = \Delta G^{o} + RT \ln Q$$

where q is the reaction quotient of the reaction.
We can substitute for ΔG and ΔG^{o} from Eqs. (11.3) and (11.4) to get

$$-nFE_{\text{cell}} = -nFE^{o}_{\text{cell}} + RT \ln Q$$

Dividing both sides by $-nF$, we get

$$E_{\text{cell}} = E^{o}_{\text{cell}} - \frac{RT \ln Q}{nF} \tag{11.5}$$

At equilibrium, when $E_{\text{cell}} = 0$, then $Q = K$. Substituting in Eq. (11.5), we get

$$E^{\circ}_{\text{cell}} = -\frac{RT}{nF}\ln K = -\frac{2.303RT}{nF}\log K \qquad (11.6)$$

Calculation of Cell Potential and Other Thermodynamic Parameters

The free energy change for a cell reaction is given by

$$\Delta G^{\circ} = -nFE^{\circ}_{\text{cell}}$$

Similarly, the changes in enthalpy and entropy of the cell reaction can also be determined if the temperature dependence of the emf of a cell is given by **Gibbs–Helmholtz** equation.

$$\Delta G = \Delta H + T\left[\frac{\partial(\Delta G)}{\partial T}\right]_p$$

Now, since $\Delta G = -nFE$, therefore,

$$\left[\frac{\partial(\Delta G)}{\partial T}\right]_p = -nF\left(\frac{\partial E}{\partial T}\right)_p$$

Therefore,

$$-nFE = \Delta H - nFT\left(\frac{\partial E}{\partial T}\right)_p$$

or

$$\Delta H = -nF\left[E - T\left(\frac{\partial E}{\partial T}\right)_p\right] \qquad (11.7)$$

Thus, ΔH of the cell reaction can be determined. Now, $\Delta G = \Delta H - T\Delta S$. Therefore,

$$\Delta S = \frac{\Delta H - \Delta G}{T} = nF\left(\frac{\partial E}{\partial T}\right)_p \qquad (11.8)$$

This gives us ΔS for the cell reaction.

Solved Example 11-8

The Edison storage cell is represented as

$$\text{Fe(s)}|\text{FeO(s)}||\text{KOH(aq)}||\text{Ni}_2\text{O}_3\text{(s)}|\text{Ni(s)}$$

The half-cell reactions are

$$\text{Ni}_2\text{O}_3\text{(s)} + \text{H}_2\text{O(l)} + 2e^- \rightarrow 2\text{NiO(s)} + 2\text{OH}^-\text{(aq)}$$
$$E^{\circ} = 0.4\ \text{V}$$

$$\text{FeO(s)} + \text{H}_2\text{O(l)} + 2e^- \rightarrow \text{Fe(s)} + 2\text{OH}^-\text{(aq)}$$
$$E^{\circ} = -0.87\ \text{V}$$

(a) What is the cell reaction?

(b) What is the cell emf? How does it depend on the concentration of KOH?

(c) What is the maximum amount of electrical energy that can be obtained from one mole of Ni_2O_3?

Solution

(a) Given cell is $\text{Fe(s)}\,|\,\text{FeO}\,|\,\text{Ni}_2\text{O}_3\text{(s)}\,|\,\text{Ni(s)}$

At the anode:

$$\text{Fe(s)} + 2\text{OH}^-\text{(aq)} \rightarrow \text{FeO(s)} + \text{H}_2\text{O(l)} + 2e^-$$
$$E^{\circ}_{\text{ox}} = 0.87\ \text{V}$$

At the cathode:

$$\mathrm{Ni_2O_3(s) + H_2O(l) + 2}e^- \rightarrow \mathrm{2NiO(s) + 2OH^-(aq)}$$

$$\underline{E^\circ_{\mathrm{red}} = 0.4\ \mathrm{V}}$$

$$\mathrm{Fe(s) + Ni_2O_3(s) \rightarrow FeO(s) + 2NiO(s)}$$

$$E^\circ_{\mathrm{cell}} = 1.27\ \mathrm{V}$$

(b) The cell emf is $E^\circ_{\mathrm{cell}} = E^\circ_{\mathrm{ox}} + E^\circ_{\mathrm{red}} = 1.27$ V. As the net reaction does not contain $\mathrm{OH^-}$, the cell emf does not depend on the concentration of KOH.

(c) The maximum amount of electrical energy is given by

$$\Delta G^\circ = -nFE^\circ_{\mathrm{cell}} = -2 \times 96500 \times 1.27$$

$$= 2.45 \times 10^5\ \mathrm{J\,mol^{-1}} = 2.45 \times 10^2\ \mathrm{kJ\,mol^{-1}}$$

Solved Example 11-9

Calculate E° for the reaction $\mathrm{Fe^{3+}} + e^- \rightarrow \mathrm{Fe^{2+}}$

Solution

Now, we have the reactions as

(a) $\mathrm{Fe^{3+}} + 3e^- \rightarrow \mathrm{Fe}$; $E^\circ_{\mathrm{Fe^{3+}/Fe}} = -0.0362$ V

(b) $\mathrm{Fe^{2+}} + 2e^- \rightarrow \mathrm{Fe}$; $E^\circ_{\mathrm{Fe^{2+}/Fe}} = -0.440$ V

(c) $\mathrm{Fe^{+}} + e^- \rightarrow \mathrm{Fe}$; $E^\circ_{\mathrm{Fe^{+}/Fe}} = ?$

Now, $\Delta G^\circ_1 - \Delta G^\circ_2 = \Delta G^\circ_3$, so we have

or $$(-n_1FE^\circ_1) - (-n_2FE^\circ_2) = -n_3FE^\circ_3$$

$$E^\circ_3 = \frac{n_1E^\circ_1 - n_2E^\circ_2}{n_3} = \frac{3 \times (-0.0361) - 2 \times (-0.440)}{1} = 0.772\ \mathrm{V}$$

Similarly, if we add two equations to get a third equation, then E° of the this equation is

$$E^\circ_3 = \frac{n_1E^\circ_1 + n_2E^\circ_2}{n_3}$$

Solved Example 11-10

If the half-cell reactions are,

$$\mathrm{Cu^{2+}} + e^- \rightarrow \mathrm{Cu^+};\quad E^\circ_{\mathrm{Cu^{2+}/Cu^+}} = 0.15\ \mathrm{V}$$

$$\mathrm{Cu^{2+}} + 2e^- \rightarrow \mathrm{Cu(s)};\quad E^\circ_{\mathrm{Cu^{2+}/Cu}} = 0.34\ \mathrm{V}$$

Calculate the E° of the following half-cell reaction

$$\mathrm{Cu^{+}} + e^- \rightarrow \mathrm{Cu(s)};\quad E^\circ_{\mathrm{Cu^{+}/Cu}} = ?$$

Solution

Given that

$$\mathrm{Cu^{+}} + \mathrm{Cu^{2+}} + e^-;\quad E^\circ_{\mathrm{Cu^{2+}/Cu^+}} = -0.15\ \mathrm{V}$$

$$\mathrm{Cu^{2+}} + 2e^- \rightarrow \mathrm{Cu(s)};\quad E^\circ_{\mathrm{Cu^{2+}/Cu}} = 0.34\ \mathrm{V}$$

Adding the above two equations, we get

$$\mathrm{Cu^{+}} + e^- \rightarrow \mathrm{Cu(s)};\quad E^\circ_{\mathrm{Cu^{+}/Cu}} = ?$$

Thus, we have $\Delta G^\circ_{\mathrm{Cu^+/Cu}} = \Delta G^\circ_{\mathrm{Cu^{2+}/Cu^+}} + \Delta G^\circ_{\mathrm{Cu^{2+}/Cu}}$

or $-n_{\mathrm{Cu^+/Cu}}FE^\circ_{\mathrm{Cu^+/Cu}} = -n_{\mathrm{Cu^{2+}/Cu^+}}E^\circ_{\mathrm{Cu^{2+}/Cu^+}} + (-n_{\mathrm{Cu^{2+}/Cu}}E^\circ_{\mathrm{Cu^{2+}/Cu}})$

Hence,

$$E^\circ_{\mathrm{Cu^+/Cu}} = \frac{-n_{\mathrm{Cu^{2+}/Cu^+}}E^\circ_{\mathrm{Cu^{2+}/Cu^+}} - n_{\mathrm{Cu^{2+}/Cu}}E^\circ_{\mathrm{Cu^{2+}/Cu}}}{n_{\mathrm{Cu^+/Cu}}}$$

$$= \frac{1 \times (-0.15) + 2 \times 0.34}{1}$$

$$= -0.15 + 0.68 = +0.53\ \mathrm{V}$$

Solved Example 11-11

If E°_1, E°_2 and E°_3 are the standard electrode potentials for Fe/$\mathrm{Fe^{2+}}$, $\mathrm{Fe^{2+}}$/$\mathrm{Fe^{3+}}$ and Fe/$\mathrm{Fe^{3+}}$ electrodes, respectively, derive a relation between E°_1, E°_2 and E°_3.

Solution

Let us consider the reduction reactions:

$$\mathrm{Fe} \rightarrow \mathrm{Fe^{2+}} + 2e^- \qquad \Delta G^\circ_1 = -nFE^\circ = -2 \times E^\circ_1 \times F \qquad (1)$$

$$\mathrm{Fe^{2+}} \rightarrow \mathrm{Fe^{3+}} + e^- \qquad \Delta G^\circ_2 = -nFE^\circ = -1 \times E^\circ_1 \times F \qquad (2)$$

$$\mathrm{Fe} \rightarrow \mathrm{Fe^{3+}} + 3e^- \qquad \Delta G^\circ_3 = -nFE^\circ = -3 \times E^\circ_3 \times F \qquad (3)$$

Subtract Eq. (1) from Eq. (3)

$$\mathrm{Fe^{2+}} \rightarrow \mathrm{Fe^{3+}} + e^- \qquad \Delta G^\circ_3 - \Delta G^\circ_1 = F(-3E^\circ_3 + 2E^\circ_1) \qquad (4)$$

Comparing Eqs. (3) and (4), we get

$$-1 \times E^\circ_2 \times F = F\ (-3E^\circ_3 + 2E^\circ_1)E^\circ_2 = 3E^\circ_3 - E^\circ_1$$

$$3E^\circ_3 = 3E^\circ_2 - E^\circ_1$$

Solved Example 11-12

Tarnished silver contains Ag_2S. Can this tarnish be removed by placing tarnished silverware in an aluminium pan containing an inert electrolytic solution such as NaCl? The standard electrode potential for the half reactions are: For $Ag_2S(s)+2e^- \rightarrow 2Ag(s)+S^{2-}$, it is –0.71 V and for $Al^{3+}+3e^- \rightarrow Al(s)$, it is –1.66 V.

Solution

The tarnished silver can be removed only if there will be reaction between Ag_2S and Al^{3+} and that too should be spontaneous.

E_{cell} is calculated as follows:

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} = -0.71-(-1.66) = 0.95 \text{ V}$$

ΔG will be negative as $\Delta G = -nFE_{\text{cell}}$. Tarnish can be removed by placing silverware in aluminium pan.

Solved Example 11-13

At 273 K, the calorimetric determination of ΔH for the reaction

$$Zn(s)+2AgCl(s) \rightarrow ZnCl_2(aq)+Ag(s)$$

yielded –217.78 kJ mol^{-1}, while the emf of the corresponding cell was 1.015 V. What is $(\partial E/\partial T)_p$ of the cell?

Solution

We know that $\Delta H = -nF\left[E - T\left(\dfrac{\partial E}{\partial T}\right)_p\right]$

Therefore,

$$\left(\frac{\partial E}{\partial T}\right)_p = \frac{1}{T}\left[E+\frac{\Delta H}{nF}\right] = \frac{1}{273}\left[(1.015)+\frac{(-217.78)}{2\times 46500}\right]$$
$$= -4.154\times 10^{-4} \text{ V K}^{-1}$$

11.5 | NERNST EQUATION

The effect of concentration on the cell potential can be obtained from thermodynamics and is given by

$$E_{\text{cell}} = E^{\text{o}}_{\text{cell}} - \frac{RT\ln Q}{nF} \tag{11.9}$$

This equation is commonly known as the **Nernst equation**, named after Walther Nernst, a German chemist and physicist. Notice, if $Q = 1$ then ln $Q = 0$ and $E_{\text{cell}} = E^{\text{o}}_{\text{cell}}$.

Consider an electrode assembly undergoing a spontaneous reaction.

$$M^{n+} + ne^- \rightleftharpoons M$$

If this system is in equilibrium, then as per law of mass action, the equilibrium constant (K) can be evaluated as

$$K = \frac{[M]}{[M^{n+}]}$$

The electrode potential of the cell at any concentration can be represented as

$$E_{M^{n+}/M} = E^{\text{o}}_{M^{n+}/M} - \frac{RT}{nF}\ln\frac{[M]}{[M^{n+}]} \tag{11.10}$$

For pure solids, [M] = 1. Therefore, Eq. (11.10) can be written as

$$E_{M^{n+}/M} = E^{\text{o}}_{M^{n+}/M} - \frac{RT}{nF}\ln\frac{1}{[M^{n+}]} \tag{11.11}$$

where R is the gas constant (8.314 J $K^{-1}mol^{-1}$), F is Faraday's constant (96,485 C mol^{-1}, but for calculation purposes, 96,500 C mol^{-1} is used), T is temperature in kelvin and $[M^{n+}]$ is the concentration of the ions. This equation is commonly known as Nernst equation. It defines the relationship of cell potential to ion concentration. In terms of natural logarithm, the equation can be expressed as

$$E = E^{o} - \frac{2.303}{nF} RT \log \frac{1}{[M^{n+}]}$$

In writing the Nernst equation for a galvanic cell, we can use the expression for mass action, using molar concentrations for ions and partial pressures (in atmosphere) for gases. Thus, for the following cell using a hydrogen electrode (with the partial pressure of H_2 not necessarily equal to 1 bar) and having the reaction

$$Cu^{2+}(aq) + H_2(g) \rightarrow Cu(s) + 2H^{+}(aq)$$

the Nernst equation would be written as

$$E_{cell} = E^{o}_{cell} - \frac{RT}{nF} \ln \frac{[H^{+}]^2}{[Cu^{2+}]p_{H_2}}$$

Note: ΔG varies with temperature, at equilibrium of the system. van't Hoff's equations bring about their relation:

$$\Delta G = \Delta G^{o} + RT \ln \frac{a_{products}}{a_{reactants}} \tag{11.12}$$

where T is the temperature on Kelvin scale and $a_{products}$ and $a_{reactants}$ are activities of products and reactants. Due to interionic attractions between the ions, they do not always behave as though their concentrations are equal to their molarities. In principle, we should use effective concentrations (called activities) in the mass action expression. However, we use molarities for the sake of simplicity because activities are difficult to calculate at this level.

Equilibrium Constant from Nernst Equation

The emf of a galvanic cell is given by a general expression:

$$E_{cell} = E^{o}_{cell} - \frac{2.303\,RT}{nF} \log Q$$

where Q is the reaction quotient. For a reaction $M(s) + N^{n-}(aq) \rightleftharpoons M^{n+}(aq) + N(s)$,

$$Q = \frac{[M^{n+}][N]}{[M][N^{n+}]} = \frac{[M^{n+}]}{[N^{n+}]}$$

as the concentration of solid M and N is taken as unity. For this reaction, the Nernst equation is

$$E_{cell} = E^{o}_{cell} - \frac{2.303\,RT}{nF} \log \frac{[M^{n+}]}{[N^{n+}]}$$

At 298 K, substituting the values of R and F, we get

$$E_{cell} = E^{o}_{cell} - \frac{0.0592}{n} \log \frac{[M^{n+}]}{[N^{n+}]}$$

For Daniell cell where reaction is $Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$, the Nernst equation is written as

$$E_{cell} = E^{o}_{cell} - \frac{2.303\,RT}{2F} \log \frac{[Zn^{2+}]}{[Cu^{2+}]} \tag{11.13}$$

If the two electrodes are connected, with the passage of time, the concentration of Zn^{2+} increases and that of Cu^{2+} decreases. The voltage of the cell keeps on declining with time, till the concentration of the Zn^{2+} and Cu^{2+} ions becomes constant and an equilibrium is achieved. Now voltmeter will give zero reading, that is, the cell potential becomes zero.

Here, the reaction quotient Q becomes equal to the equilibrium constant K_{eq}. Equation (11.13) can be written as

$$0 = E^{o}_{cell} - \frac{2.303\,RT}{nF}\log K_{eq} \qquad \left(\text{where } K_{eq} = \frac{[Zn^{2+}]}{[Cu^{2+}]}\right)$$

or

$$E^{o}_{cell} = \frac{2.303\,RT}{nF}\log K_{eq} \tag{11.14}$$

As $E^{o}_{cell} = 1.1$ V, we have

$$\log\ K_{eq} = \frac{2\,F \times 1.1\text{ V}}{2.303\,RT}$$

At 298 K, substituting the values of R and F, we get

$$\log K_{eq} = \frac{2 \times 1.1}{0.0591} = 37.22$$

Taking antilog, we get $K_{eq} = 1.65 \times 10^{37}$. Such a high value of K_{eq} indicates that at equilibrium most of the Cu^{2+} ions are converted into Cu (since we know that $K_{eq} = [Zn^{2+}]/[Cu^{2+}]$).

Note:

1. Any half-cell reaction will always have e^- term.
2. Any full-cell reaction will never have any e^- term.
3. n is the number of electrons in case of a half-cell reaction. For example, consider the half-cell reactions

$$\text{Ag} \rightleftharpoons \text{Ag}^+ + 1e^- \qquad (n = 1)$$
$$\text{Cu}^{2+} + 2e^- \rightleftharpoons \text{Cu} \qquad (n = 2)$$

The number of electrons is cancelled in case of full-cell reaction.

$$2\text{Ag} + \text{Cu}^{2+} \rightleftharpoons \text{Cu} + 2\text{Ag}^+ \qquad (n = 2)$$

4. At 25 °C, Nernst equation is

$$E_{cell} = E^{o}_{cell} - \frac{0.059}{n}\log Q$$

Applications of Nernst Equation

The Nernst equation is a useful tool in electrochemistry and has the following applications:

1. The potential of an electrode and emf of a cell can be calculated at any temperature and concentration.
2. Knowing potential of an electrode, the concentration of the reactant can be calculated.
3. The concentration of a solution in the galvanic cell can be determined.
4. Knowing the emf of a cell, the equilibrium constant of the cell reaction can be calculated.

These applications are illustrated with the help of the following solved examples.

Solved Example 11-14

Calculate the electrode potential of copper, if the concentration of $CuSO_4$ is 0.206 M at 23.1°C. Given that $E^o_{Cu^{2+}/Cu} = +0.34$ V.

Solution

Given that $[CuSO_4] = 0.206$ M; $T = 296.1$ K. The reaction taking place is

$$Cu^{2+} + 2e^- \rightleftharpoons Cu \text{ where } n = 2$$

According to Nernst's equation,

$$E_{Cu^{2+}/Cu} = E^o_{Cu^{2+}/Cu} - \frac{2.303RT}{nF}\log\frac{1}{[Cu^{2+}]}$$

or

$$E_{Cu^{2+}/Cu} = +0.34 - \frac{2.303\times 8.314\times 296.1}{2\times 96,500}\times\log\frac{1}{0.206}$$

$$= 0.31984 \text{ V}$$

Solved Example 11-15

Calculate the emf of the following Zn–Ag cell at 22.3°C if the concentration of $ZnSO_4$ and $AgNO_3$ are 0.191 M and 0.0289 M, respectively. Given that $E^o_{Zn^{2+}/Zn} = -0.76$ V and $E^o_{Ag^+/Ag} = +0.8$ V

Solution

Here $E^o_{Zn^{2+}/Zn} < E^o_{Ag^+/Ag}$. Hence, zinc electrode is an oxidation electrode, while silver electrode is a reduction electrode. The cell representation is

$$Zn|ZnSO_4(0.191 M)\,||\,Ag^+(0.0289 M)\,|\,Ag$$

The reaction occurring in the cell is
Oxidation electrode: $Zn \rightleftharpoons Zn^{2+} + 2e^-$
Reduction electrode: $(Ag^+ + e^- \rightleftharpoons Ag)\times 2$

The overall cell reaction: $Zn + 2Ag^+ \rightleftharpoons Zn^{2+} + Ag$

Therefore, $Q = \dfrac{[Zn^{2+}]}{[Ag^+]^2}$

where Q represents the quotient of reactant and products. According to Nernst equation,

$$\begin{aligned}
E_{cell} &= E^o_{cell} - \frac{2.303RT}{nF}\log Q \\
&= [E^o_{Ag^+/Ag} - E^o_{Zn^{2+}/Zn}] - \frac{2.303RT}{nF}\log Q \\
&= [+0.8 - (-0.76)] - \frac{2.303\times 8.314\times 295.3}{2\times 96,500}\log\frac{[Zn^{2+}]}{[Ag^+]^2} \\
&= +1.56 - \frac{2.303\times 8.314\times 295.3}{2\times 96,500}\log\frac{0.191}{(0.0289)^2} \\
&= 1.4908 \text{ V}
\end{aligned}$$

Solved Example 11-16

Calculate the concentration of $NiCl_2$ in the nickel electrode having a potential of 0.16942 V at 24.9°C. Given that $E^o_{Ni^{2+}/Ni} = -0.14$ V.

Solution

Applying the Nernst equation,

$$E_{Ni^{2+}/Ni} = E^o_{Ni^{2+}/Ni} - \frac{2.303RT}{nF}\log\frac{1}{[Ni^{2+}]}$$

Here $n = 2$. So,

$$-0.16942 = -0.14 + \frac{2.303\times 8.314\times 297.9}{2\times 96.500}\log(x);$$

where $x = [Ni^{2+}]$. So,

$$-0.16942 = -0.14 + (0.02955)\log x$$
$$-0.02942 = 0.02955\log x$$

we get $x = [Ni^{2+}] = 0.1010$
So, concentration of $NiCl_2$ is 0.1010 M.

Solved Example 11-17

A hydrogen electrode is immersed in a 0.10 M solution of acetic acid at 25°C. The electrode is connected to another consisting of an iron nail dipping into 0.10 M $FeCl_2$. What will be the measured potential of this cell? Assume $p_{H_2} = 1.00$ atm.

Solution

The oxidation reaction is:

$$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s) \quad E^o_{Fe^{2+}/Fe} = -0.44\ V$$

The reduction reaction is:

$$2H^+(aq) + 2e^- \rightarrow H_2(g) \quad E^o_{H^+/\frac{1}{2}H_2} = 0.00\ V$$

The overall cell reaction is:

$$2H^+(aq) + Fe(s) \rightarrow H_2(g) + Fe^{2+}(aq) \quad E^o_{cell} = 0.44\ V$$

$$E_{cell} = E^o_{cell} - \frac{0.0592}{n}\log\frac{[Fe^{2+}]}{[H^+]^2}$$

where $[Fe^{2+}] = 0.10$ M and $[H^+]$ is from the ionization of acetic acid.

Now, $$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = 1.8 \times 10^{-5}$$

If $[H^+] = x$ and $[CH_3COO^-] = x$, then $[CH_3COOH] = 0.10 - x$. Substituting, we get

$$1.8 \times 10^{-5} = \frac{[x][x]}{[0.10 - x]}$$

Assuming x is small compared to the concentration of CH_3COOH, we get

$$x = 1.34 \times 10^{-3}\ M = [H^+] = [CH_3COO^-] \text{ and } [CH_3COOH] = 0.10\ M$$

Now, we know that $n = 2$, so from Nernst equation, we have

$$E_{cell} = 0.44 - \frac{0.0592}{2}\log\frac{[0.10]}{(1.34 \times 10^{-3})^2}$$
$$= 0.44 - 0.14 = 0.30\ V$$

Solved Example 11-18

The value of K_{sp} for AgBr is 5.0×10^{-13}. What will be the potential of a cell constructed of a standard hydrogen electrode as one half-cell and a silver wire coated with AgBr dipping into 0.10 M HBr as the other half-cell? For the Ag/AgBr electrode,

$$AgBr(s) + e^- \rightleftharpoons Ag(s) + Br^-(aq); \quad E^o_{AgBr} = +0.070\ V$$

Solution

The concentration of Br^- in solution is 0.10 M. Since the K_{sp} of AgBr is so small, the amount of dissociation of AgBr from the electrode will be negligible.
The reduction reaction is

$$AgBr(s) + e^- \rightleftharpoons Ag(s) + Br^-(aq); \quad E^o_{AgBr} = +0.070\ V$$

The oxidation reaction is

$$H_2 \rightarrow 2H^+ + 2e^-; \quad E^o_{\frac{1}{2}H_2/H^+} = 0.00\ V$$

The net cell reaction is

$$2AgBr(s) + H_2 \rightleftharpoons 2Ag(s) + 2Br^-(aq) + 2H^+(aq)$$
$$E^o_{cell} = 0.070\ V$$

The potential for the constructed cell is calculated using the Nernst equation is

$$E_{cell} = E^o_{cell} - \frac{0.0592}{n}\log\frac{[Br^-]^2}{[H^+]^2} = 0.070 - \frac{0.0592}{2}\log\frac{(0.1)^2}{(1)^2}$$
$$= 0.070 - (-0.0592) = 0.129\ V$$

Solved Example 11-19

Consider the following galvanic cell

$$Ag(s)|Ag^+(0.00030\ M)||Fe^{3+}(0.0011\ M), Fe^{2+}(0.040\ M)$$
$$|Pt(s)$$

Calculate the cell potential. Determine the sign of the electrodes in the cell. Write the equation for the spontaneous cell reaction.

Solution

The half-cell reaction at anode is

$$Ag(s) \rightarrow Ag^+(aq) + e^-; \quad E^o = -0.80\ V$$

The half-cell reaction at cathode is

$$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq) \quad E^o = 0.77\ V$$

Now, $E^o_{cell} = E^o_{red} - E^o_{ox} = 0.77 - 0.80 = -0.03$ V. Therefore,

$$E_{cell} = E^o_{cell} - \frac{0.0592}{1}\log\frac{[Fe^{2+}][Ag^+]}{[Fe^{3+}]}$$
$$= -0.03 - \frac{0.0592}{1}\log\frac{(3.0 \times 10^{-4})(4.0 \times 10^{-2})}{(1.1 \times 10^{-3})}$$
$$= 0.09\ V$$

As stated, being a galvanic cell, and using conventions in cell notation, the left-side half-cell is the anode and negatively charged, and the right-side half-cell is the cathode and positively charged. The equation for the spontaneous cell reaction is

$$Fe^{3+}(1.1\times10^{-3}\ M) + Ag(s) \rightarrow Ag^{+}\ (3.0 \times 10^{-4}\ M) + Fe^{2+}(0.040\ M)$$

This is an example of a concentration cell.

Solved Example 11-20

The standard reduction potential for the half-cell reaction $NO_3^-(aq) + 2H^+(aq) + e^- \rightarrow NO_2(g) + H_2O(l)$ is 0.78 V.

(a) Calculate the reduction potential in H^+ (8 M).

(b) What will be the reduction potential of the half cell in a neutral solution? Assume all the other species to be at unit concentration.

Solution

The given reaction is

$$NO_3^-(aq) + 2H^+(aq) + e^- \rightarrow NO_2(g) + H_2O(l)$$

Writing Nernst equation for the above reaction, and substituting concentration of pure liquids as 1, we get

$$E_{cell} = E^o_{cell} - \frac{0.0591}{n}\log\frac{[NO_2][H_2O]}{[NO_3][H^+]}$$

$$= 0.78 - \frac{0.0591}{1}\log\frac{1\times1}{1\times(8)^2}$$

$$= 0.78 + 0.0591\times2\log8$$

$$= 0.78 + 0.106 = 0.8867\ V$$

(b) pH = 7 for a neutral solution. As pH = –log $[H^+]$ so $[H^+] = 10^{-7}$. Now, E_{cell} can be found as

$$E_{cell} = \frac{0.0591}{1}\ \log\ \frac{1}{(10^{-7})^2} = -0.0474\ V$$

Solved Example 11-21

Calculate the equilibrium constant for the reaction, $2Fe^{3+} + 3I^- \rightleftharpoons 2Fe^{2+} + I_3^-$. The standard reduction potentials in acidic conditions are 0.77 V and 0.54 V, respectively, for Fe^{3+}/Fe^{2+} and I_3^-/I^- couples.

Solution

The reaction involved is

$$2Fe^{3+}(aq) + 3I^-(aq) \rightleftharpoons 2Fe^{2+}(aq) + I_3^-(aq)$$

and the E^o_{cell} is given by $E^o_{cell} = E^o_{cathode} - E^o_{anode}$. Also,

$$E^o_{cell} = \frac{0.0591}{n\ \log K}$$

Substituting values, we get

$$0.23 = \frac{0.0591}{2\ \log K}$$

Therefore,

$$\log K = 7.7834 \Rightarrow K = \text{antilog}\ (7.7834) = 6.073\times10^7$$

Solved Example 11-22

Calculate the pH of the half-cell: Pt, $H_2|H_2SO_4$. The oxidation electrode potential is + 0.3 V.

Solution

Given that oxidation potential = 0.3 V. So, reduction potential = –oxidation potential = –0.3 V

The cell reaction is $2H^+(aq) + 2e^- \rightarrow H_2(g)$. Using Nernst equation, we get

$$E_{cell} = E^o_{cell} - \frac{0.0591}{n}\log\frac{1}{[H^+]^2}$$

or

$$-0.3 = 0 - \frac{0.0591}{2}(-2\log[H^+])$$

Now, as $pH = -\log[H^+]$, we have

$$-0.3 = -0.0591\ pH \Rightarrow pH = \frac{0.3}{0.0591} = 5.076$$

Solved Example 11-23

The EMF of a cell corresponding to the reaction $Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(0.1\,M) + H_2(g, 1\,atm)$ is 0.28 V at 25°C. Write the half-cell reactions and calculate the pH of the solution at the hydrogen electrode. Given $E^o_{Zn} = 0.76$ V and $E^o_{H_2} = 0$.

Solution

Half-cell reactions are as follows:

At anode: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

At cathode: $2H^+(aq) + 2e^- \rightarrow H_2(g)$

According to Nernst equation,

$$E_{Zn} = E^o_{Zn} - \frac{0.0591}{n}\log\frac{[Zn^{2+}]}{[Zn]}$$

Substituting given values, we get

$$E_{Zn} = 0.76 - \frac{0.0591}{n}\log[0.1] = 0.76 - 0.0295 \times -1$$

$$= 0.76 + 0.0295 = 0.76895\,V$$

$$E_{H_2} = E^o_{H_2} - \frac{0.0591}{n}\log\frac{[H_2]}{[H^+]^2} = 0 - 0.0591\log[H^+]$$

$$= -0.0591\text{ pH}$$

Therefore, the pH is calculated as

$$E_{cell} = E_{Zn} + E_{H_2} \Rightarrow 0.28 = 0.76 - 0.0591\,\text{pH}$$

or $$\text{pH} = \frac{0.76 - 0.28}{0.591} = 8.12$$

Solved Example 11-24

Find the equilibrium constant for the reaction $Cu^{2+} + In^{2+} \rightleftharpoons Cu^+ + In^{2+}$ Given that $E^o_{Cu^{2+}/Cu^+} = 0.15$ V, $E^o_{In^{2+}/In^+} = -0.4$ V, $E^o_{In^{3+}/In^+} = -0.42$ V. **(IIT-JEE 2004)**

Solution

We know that $\Delta G = -nFE^o_{cell}$. Thus, we have three reactions as

$$\begin{aligned}
&Cu^{2+}(aq) + e^- \rightarrow Cu^+(aq) && \Delta G^o_1 = -0.15\,F\\
&In^{2+}(aq) + e^- \rightarrow In^+(aq) && \Delta G^o_2 = +0.4\,F\\
&In^+(aq) \rightarrow In^{3+}(aq) + 2e^- && \Delta G^o_3 = -2 \times 0.42\,F = 0.84\,F
\end{aligned}$$

Adding all the equations, we get

$$Cu^{2+}(aq) + In^{2+}(aq) \rightarrow Cu^+(aq) + In^{3+}(aq)$$

and $\Delta G^o = -nFE^o = (-0.15 + 0.4 - 0.84)\,F = -0.59\,F$. As $n = 1$, we get

$$-0.59\text{ F} = -FE^o_{cell} \Rightarrow E^o_{cell} = 0.59\text{ V}$$

Now, using Nernst equation, we can find the equilibrium constant as

$$E_{cell} = E^o_{cell} - \frac{0.0591}{n}\log K_C$$

where $E_{cell} = 0$ at equilibrium. So, we have

$$0.59 = \frac{0.0591}{1}\log K_C \Rightarrow K_C = 10^{10}$$

Solved Example 11-25

Determine the concentration of Cd^{2+} ions in the following electrochemical cell:

$$Fe|Fe^{2+}(0.1\text{ M})||Cd^{2+}(x\text{ M})|Cd$$

Given that $E_{cell} = -0.02$ V and $E^o = 0.04$ V at 298 K.

Solution

According to Nernst equation, for the cell reaction $Fe(s) + Cd^{2+}(aq) \rightarrow Fe^{2+}(aq) + Cd(s)$

$$E_{cell} = E^o_{cell} - \frac{0.0591}{n}\log\frac{[Fe^{2+}][Cd]}{[Fe][Cd^{2+}]}$$

Substituting given values, we get

$$-0.02 = 0.04 - \frac{0.0591}{2}\log\frac{[0.1]}{[x]} \Rightarrow -0.06 = -\frac{0.0591}{2}\log\frac{[0.1]}{[x]}$$

$$2.03 = \log\frac{[0.1]}{[x]} \Rightarrow 2.03 = -1 - \log[x] \Rightarrow 3.03 = -\log[x]$$

$$\log x = -3.03$$

On taking antilog, we get $x = 0.00093$ M.

Solved Example 11-26

Consider the disproportionation $2\text{Cu}^+ \rightleftharpoons \text{Cu}^{2+} + \text{Cu(s)}$. At equilibrium, the value of $[\text{Cu}^{2+}]/[\text{Cu}^+]^2 = 1.8 \times 10^6$. If $E^\circ_{\text{Cu}^{2+}/\text{Cu}^+} = +0.15$ V, calculate $E^\circ_{\text{Cu}^+/\text{Cu}}$.

Solution

We know that at equilibrium, $E_{\text{cell}} = 0$, so

$$E^\circ_{\text{cell}} = \frac{0.0591}{n}\log\frac{[\text{Cu}^{2+}]}{[\text{Cu}^+]^2}$$

Given that $[\text{Cu}^{2+}]/[\text{Cu}^+]^2 = 1.8 \times 10^6$, so we have

$$E^\circ_{\text{Cu}^+/\text{Cu}^{2+}} + E^\circ_{\text{Cu}^+/\text{Cu}} = \frac{0.591}{1}\log(1.8 \times 10^6)$$

or $\quad -0.15 + E^\circ_{\text{Cu}^+/\text{Cu}} = 0.3697$

Solving, we get $\quad E^\circ_{\text{Cu}^+/\text{Cu}} = +0.5197\ \text{V}$.

11.6 | CALCULATION OF E°_{CELL}

For calculation of E°_{cell}, let us consider the following cases.

1. **When two half-cells combine to give a full cell:** Consider the following half-cells.

$$\text{Zn} \,|\, \text{Zn}^{2+} \,||\, \text{Cu}^{2+} \,|\, \text{Cu}$$

Given that:

$$E^\circ_{\text{Zn}^{2+}/\text{Zn}} = x = \text{SRP}_{\text{cathode}}$$
$$E^\circ_{\text{Cu}^{2+}/\text{Cu}} = y = \text{SRP}_{\text{anode}}$$

Reactions taking place are:

At the cathode: $\text{Cu}^{2+} + 2e^- \rightleftharpoons \text{Cu} \qquad E^\circ = y$

At the anode: $\text{Zn} \rightleftharpoons \text{Zn}^{2+} + 2e^- \qquad E^\circ = -x$

Full cell reaction: $\text{Cu}^{2+} + \text{Zn} \rightleftharpoons \text{Zn}^{2+} + \text{Cu} \qquad E^\circ_{\text{cell}} = y - x$

Thus, $E^\circ_{\text{cell}} = \text{SRP}_{\text{cathode}} - \text{SRP}_{\text{anode}}$

Now consider the example of following half-cells.

$$\text{Ag} \,|\, \text{Ag}^{+} \,||\, \text{Zn}^{2+} \,|\, \text{Zn}$$

Given that:

$$E^\circ_{\text{Ag}^{+}/\text{Ag}} = x = \text{SRP}_{\text{cathode}}$$
$$E^\circ_{\text{Zn}^{2+}/\text{Zn}} = y = \text{SRP}_{\text{anode}}$$

Reactions taking place are:

At the cathode: $\text{Zn}^{2+} + 2e^- \rightleftharpoons \text{Zn} \qquad E^\circ = y$

At the anode: $(\text{Ag} \rightleftharpoons \text{Ag}^+ + 1e^-) \times 2 \qquad E^\circ = -x$

Full cell reaction: $2\text{Ag} + \text{Zn}^{2+} \rightleftharpoons 2\text{Ag}^+ + \text{Zn} \qquad E^\circ_{\text{cell}} = y - x$

Thus, $E^\circ_{\text{cell}} = \text{SRP}_{\text{cathode}} - \text{SRP}_{\text{anode}} = y - x$

Note: In the above question, we do not multiply E° by 2, as it is an intensive property.

2. **When two half-cells combine to give another half-cell:** Consider the example of the following half-cells. Given that:

$$E^\circ_{\mathrm{Fe^{3+}/Fe^{2+}}} = x$$
$$E^\circ_{\mathrm{Fe^{2+}/Fe}} = y$$

Then for calculating $E^\circ_{\mathrm{Fe^{3+}/Fe}}$, we will add ΔG°'s and not value of E°'s. The half-cell reactions are:

$$\mathrm{Fe^{3+}} + e^- \rightleftharpoons \mathrm{Fe^{2+}} \qquad E_1^\circ = x,\ n = 1 \tag{11.15}$$
$$\mathrm{Fe^{2+}} + 2e^- \rightleftharpoons \mathrm{Fe} \qquad E_2^\circ = y,\ n = 2 \tag{11.16}$$
$$\mathrm{Fe^{3+}} + 3e^- \rightleftharpoons \mathrm{Fe} \qquad E_3^\circ = ?,\ n = 3 \tag{11.17}$$

We can see that,
Eq. (11.15) + Eq. (11.16) = Eq. (11.17). Therefore,

$$\Delta G_1^\circ + \Delta G_2^\circ = \Delta G_3^\circ \qquad (\text{as } \Delta G^\circ \text{ is a state function})$$

Therefore,

$$-n_1FE_1^\circ - n_2FE_2^\circ = -n_3FE_3^\circ$$
$$E_3^\circ = \frac{n_1FE_1^\circ + n_2FE_2^\circ}{n_3} = \frac{1\times x + 2\times y}{3}$$

11.7 | TYPES OF ELECTRODES

Electrodes of a galvanic cell can consist of different components or constituents. Based on the constituents, they are classified as follows:

1. **Metal–Metal ion half-cell:** In this case, a metal rod is dipped in an electrolytic solution of the corresponding metal ion having concentration C M. It can be made to act as anode as well as cathode (Fig. 11.7).

   Half-cell reaction at the anode: $\mathrm{M(s)} \rightarrow \mathrm{M^{n+}(aq)} + ne^-$

   Half-cell reaction at the cathode: $\mathrm{M^{n+}(aq)} + ne^- \rightarrow \mathrm{M(s)}$

   For example, $\mathrm{Sn^{2+}/Sn}$, $\mathrm{Zn^{2+}/Zn}$, $\mathrm{Ag^+/Ag}$, etc.

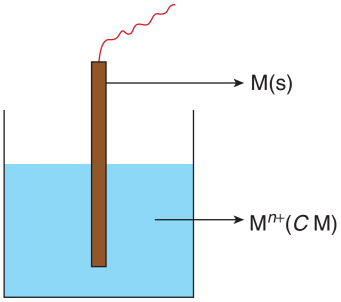


Figure 11.7 Metal–metal ion half-cell.

2. **Gas–Gas ion half-cell:** It consists of a noble metal like platinum which is simultaneously in contact with a gas and a solution of ions of the gas. Since gases cannot conduct electricity, an inert metal is used to make electrical contact. The metal helps in establishing the equilibrium. The potential of the electrode depends on the pressure of the gas and the activity of the solution. For example, a gas is bubbled into its gas ion solution with a platinum rod coated with platinum black dipped for making electrical contact as gas is non-conducting (Fig. 11.8). For example,

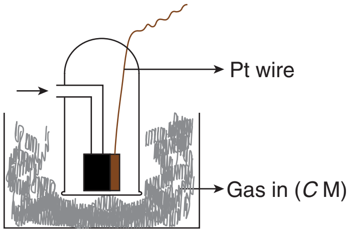


Figure 11.8 Gas–gas ion half-cell.

$$\mathrm{Pt|H_2}(p\ \mathrm{atm})|\mathrm{H^+}(C\ \mathrm{M})$$
$$\mathrm{Pt|O_2}(p\ \mathrm{atm})|\mathrm{OH^-}(C\ \mathrm{M})$$
$$\mathrm{H^+}\ (C\ \mathrm{M}|\mathrm{O_2}(p\ \mathrm{atm})|\mathrm{OH^-}(C\ \mathrm{M})$$
$$\mathrm{H^+}\ (C\ \mathrm{M})|\mathrm{H_2}(p\ \mathrm{atm})|\mathrm{Pt}$$

The SHE is of this type, having concentration of 1 M and the pressure of H_2 gas is 1 atm.

Half-cell reaction at the anode: $H_2(p\ \text{atm}) \rightarrow 2H^+$

Half-cell reaction at the cathode: $2H^+\ (C\ \text{M}) + 2e^- \rightarrow H_2(p\ \text{atm})$

3. **Redox half-cell:** In this electrode, the electrode potential results due to the presence of ions of the same substance present in different oxidation states. For example, a platinum rod is dipped in a solution containing two different oxidation states of a metal ion (M^{x_1+} and M^{x_2+}) as shown in Fig. 11.9. For example, the quinhydrone electrode which can be used to measure the hydrogen ion concentration (pH) of a solution. The quinhydrone is slightly water soluble, and dissolves to form a mixture of quinone and hydroquinone in equal concentration. Each one of the two substances can easily be oxidized or reduced to the other. Another example is $\text{Pt}|\text{Fe}^{2+}\ (C_1\ \text{M}),\ \text{Fe}^{3+}\ (C_2\ \text{M})$ and $\text{Pt}|\text{Sn}^{2+}\ (C_1\ \text{M}),\ \text{Sn}^{4+}\ (C_2\ \text{M})$, etc.

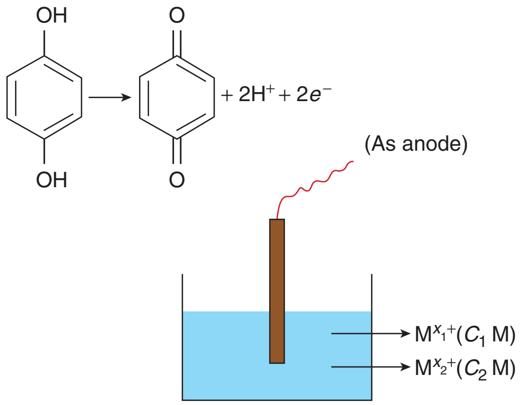


Figure 11.9 Redox half-cell.

4. **Metal insoluble–metal salt anion half-cell:** This half-cell is made by dipping a rod of silver coated with a paste of saturated AgCl at the bottom, in a solution of ionic electrolyte such as NaCl, etc. Care should be taken that the cation of electrolyte has lower standard reduction potential than that of cation of metal salt (Fig. 11.10).

   The reactions are as follows:

   (a) $\text{AgCl(s)} \rightleftharpoons \text{Ag}^+\text{(aq)} + \text{Cl}^-\text{(aq)}$

   (b) $\text{Ag}^+\text{(aq)} + e^- \rightleftharpoons \text{Ag(s)}$

   (c) $\text{AgCl(s)} + e^- \rightleftharpoons \text{Ag(s)} + \text{Cl}^-\text{(aq)}$

   If Gibbs energy change for half-cell reactions is ΔG_1° and ΔG_2°, respectively, then Gibbs energy change for the cell reaction is $\Delta G_3^\circ = \Delta G_1^\circ + \Delta G_2^\circ$.

$$-FE^\circ_{\text{Cl}^-/\text{AgCl}/\text{Ag}} = -RT\ln K_{\text{sp}} - FE^\circ_{\text{Ag}^+/\text{Ag}}$$

   Dividing throughout the equation by $-F$, we get

$$\frac{RT}{F}\ln K_{\text{sp}} + E^\circ_{\text{Ag}^+/\text{Ag}} = E^\circ_{\text{Cl}^-/\text{AgCl}/\text{Ag}}$$

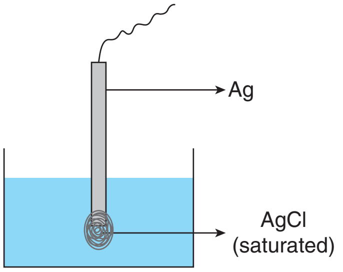


Figure 11.10 Metal insoluble–metal salt anion half-cell.

Therefore,

$$E^\circ_{\text{Cl}^-/\text{AgCl}/\text{Ag}} = E^\circ_{\text{Ag}^+/\text{Ag}} - \frac{RT}{F}\ln\frac{[\text{Cl}^-]}{K_{\text{sp}}} \tag{11.18}$$

5. **Amalgam electrode:** Amalgam is the alloy of any metal with mercury. An amalgam electrode is a modification of metal–metal ion electrode. In place of a metal, its solution in mercury is used. A typical example of zinc amalgam electrode is represented as:

$$\text{Zn(Hg)}\,|\,\text{Zn}^{2+}(x\ \text{M})$$

   The electrode reaction is

$$\text{Zn}^{2+}(x\ \text{M}) + 2e^- \rightleftharpoons \text{Zn(Hg)}$$

   According to Nernst equation, the potential of the electrode is

$$E = E^\circ_{\text{Zn}^{2+}|\text{Zn}} - \frac{2.303RT}{nF}\log\frac{[\text{Zn}]}{[\text{Zn}^{2+}]}$$

   where $[\text{Zn}^{2+}]$ and [Zn] are the concentrations of Zn^{2+} ions and Zn metal in the amalgam.

11.8 | CONCENTRATION CELLS

A concentration cell is a galvanic cell which generates electrical energy at the expense of chemical energy. In general, a concentration cell is a galvanic cell in which both electrodes contain the same electrode material, the same electrolyte but with different concentrations. These cells are classified into two types: electrode concentration cells and electrolyte concentration cells.

Electrode Concentration Cells

In these cells, the concentration of the electrolyte is the same. The two electrodes contain the same substance but with different concentration. Consider the two hydrogen electrodes having hydrogen gas at different pressures, dipped in the same electrolytic solution. The cell can be represented as

$$\text{Pt, } H_2(p_1)\,|\,\text{HCl}(x\text{ M})\,|\,H_2(p_2),\text{Pt}$$

where p_1 and p_2 are the pressures at which H_2 gas is maintained in the cell. Here, p_1 is greater than p_2. The reactions at the electrodes are:

At the anode: $H_2(p_1) \rightleftharpoons 2H^+(aq) + 2e^-$

At the cathode: $2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$

Overall cell reaction: $H_2(p_1) \rightleftharpoons H_2(p_2)$

None of these reactions involve the concentration of the electrolyte. Hence, the emf generated is independent of the concentration of the electrolyte. According to Nernst equation,

$$E_{\text{cell}} = E^{\text{o}}_{\text{cell}} - \frac{2.303RT}{nF}\log\frac{p_2}{p_1}$$

But $E^{\text{o}}_{\text{cell}} = 0$, as the electrodes are hydrogen electrodes. So,

$$E_{\text{cell}} = \frac{2.303RT}{nF}\log\frac{p_1}{p_2} \tag{11.19}$$

The other example of electrode concentration cell is

$$\text{Hg} - \text{Pb}(C_1)\,|\,\text{PbSO}_4(\text{aq})\,|\,\text{Hg} - \text{Pb}(C_2)$$

Electrolyte Concentration Cells

In these cells, the electrodes contain different concentration of the same electrolyte. The two electrodes are connected directly through a diffusion membrane. Salt bridge is not required for the completion of the cell.

$$\text{Pt, } H_2(1\text{ atm})\,|\,\text{HCl}(a_1)\,||\,\text{HCl}(a_2)\,|\,H_2(1\text{ atm}),\text{Pt}$$

The dashed line indicates the direct contact between the electrodes or through a membrane. The reactions at the electrodes are:

At the anode: $\frac{1}{2}H_2(g) \rightleftharpoons H^+(a_1) + e^-$

At the cathode: $H^+(a_2) + e^- \rightleftharpoons \frac{1}{2}H_2(g)$

Overall cell reaction: $H^+(a_2) \rightleftharpoons H^+(a_1)$

As there is direct contact between the electrodes, the ions are free to move. H^+ ions move from oxidation electrode to reduction electrode, while Cl^- ions move in the opposite direction. If $t_+ \times t_-$ are the transport numbers of H^+ and Cl^-, respectively, then the EMF of the cell is

$$E_{\text{cell}} = t - \frac{2.303RT}{nF}\log\frac{a_2}{a_1} \tag{11.20}$$

For all practical purposes, $a_2 \simeq C_2;\ a_1 \simeq C_1$.

Applications of Concentration Cells

Concentration cells are not used as a source of electrical energy, as the emf drastically decreases with time. It appears to be a theoretical concept, but has indirect applications. The principle of concentration cells is used to understand the various corrosion reactions.

Determination of Valency of Ions

A concentration cell containing different concentrations of the same ion whose valency is to be verified is constructed. The EMF of the cell is measured using the expression for EMF, and valency of the ion (n) can be calculated.

$$E_{\text{cell}} = \frac{2.303RT}{nF}\log\frac{C_2}{C_1} \tag{11.21}$$

Valency of ions like mercurous ions can be determined by constructing a concentration cell:

$$\text{Hg(l)}\,|\,\text{Hg(NO}_3)_2 \text{ in dil. HNO}_3(C_1\text{ M})\,||\,\text{Hg(NO}_3)_2\text{ in dil. HNO}_3(C_2\text{ M})\,|\,\text{Hg(l)}$$

On substituting the E_{cell} value in Eq. (11.19), the value of n can be calculated. In a mercurous nitrate concentration cell, the valency calculated will be 2. This indicates that the mercurous nitrate contains Hg_2^{2+} ions.

Solved Example 11-27

Calculate the valency of copper from the following cell at 294 K, if the emf of the cell is 0.02571 V.

$$\text{Zn}\,|\,\text{ZnSO}_4(0.00162\text{ M})\,||\,\text{ZnSO}_4(0.123\text{ M})\,|\,\text{Zn}$$

Solution

The EMF is given by $E_{\text{cell}} = \dfrac{2.303RT}{nF}\log\dfrac{C_2}{C_1}$

where $C_2 = 0.0123$ M and $C_1 = 0.00162$ M. So,

$$0.02571 = \frac{2.303\times 8.314\times 294}{n\times 96500}\cdot\log\frac{0.0123}{0.00162}$$

we get $n = 1.9975 \simeq 2.0$.

Hence, copper is in divalent state.

Determination of the Solubility of a Sparingly Soluble Salt

AgCl is sparingly soluble in water. As the solubility of AgCl is the least, it can be determined by measuring the EMF. A small quantity of freshly prepared AgCl is added to a solution of (say) 0.01 M KCl and stirred till a saturated solution is obtained. A silver rod is dipped in it. This electrode is coupled with another silver electrode. The representation of the cell is

$$\text{Ag(s)}\,|\,\text{AgCl(sat.) in KCl (0.01 M)}\,||\,\text{AgNO}_3(0.01\text{ M})\,|\,\text{Ag(s)}$$

The EMF of the cell is measured directly using VTVM (E_{cell}). For a concentration cell,

$$E_{\text{cell}} = \frac{2.303RT}{nF}\log\frac{C_2}{C_1}$$

At $T = 298$ K,

$$E_{\text{cell}} = \frac{0.0591}{n}\log\frac{C_2}{x}$$

where $x = C_1$ concentration of the saturated solution, $C_2 = 0.1$ M, $n = 1$ and $F = 96{,}500$ C. From these values, x can be calculated.

Now, AgCl is a binary salt $\quad \text{AgCl} \rightleftharpoons \text{Ag}^+ + \text{Cl}^-$

So, x M AgCl contains x mol dm^{-3} of Ag$^+$ and x mol dm^{-3} of Cl$^-$. But it is dissolved in 0.1 M KCl, so

$$[\text{Ag}^+] = x\text{ mol dm}^{-3} \quad\text{and}\quad [\text{Cl}^-] = (x+0.1)\text{ mol dm}^{-3}$$

If K_{sp} is the solubility product of AgCl then, $K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-]$

Solubility of AgCl is $\quad S_{\text{AgCl}} = \sqrt{K_{\text{sp}}} = \sqrt{[\text{Ag}^+][\text{Cl}^-]}$

Therefore, $S_{\text{AgCl}} = \sqrt{x(0.1+x)}$ mol dm^{-3} $= \sqrt{x(0.1+x)}\times 143.5$ g dm^{-3} as molecular mass of AgCl is 143.5 g mol^{-1}.

Solved Example 11-28

Two students make Daniell cells in laboratory. They take $ZnSO_4$ from common stock with Cu as positive electrode. The emf of one cell is 0.03 V more than the other. The concentration of $CuSO_4$ in cell of higher emf is 0.5 M. Find the concentration of $CuSO_4$ in the second cell. [Given that $(2.303\ RT)/F = 0.06$ V.] **(IIT-JEE 2003)**

Solution

From the reaction $Zn + Cu^{2+} \rightleftharpoons Zn^{2+} + Cu$, we have

For the first cell: $E_1 = E_1^o - \dfrac{2.303\,RT}{2\,F}\log\dfrac{[Zn^{2+}]}{[Cu^{2+}]^1}$

For the second cell: $E_2 = E_1^o - \dfrac{2.303\,RT}{2\,F}\log\dfrac{[Zn^{2+}]}{[Cu^{2+}]^2}$

Subtracting E_2 from E_1, we get

$$E_2 - E_1 = E_1^o - \frac{2.303RT}{2F}\log\frac{[Zn^{2+}]}{[Cu^{2+}]_2} - E_1^o + \frac{2.303RT}{2F}\log\frac{[Zn^{2+}]}{[Cu^{2+}]_1}$$

or $$E_2 - E_1 = \frac{2.303RT}{2F}\left[\log\frac{[Zn^{2+}]}{[Cu^{2+}]_1} - \log\frac{[Zn^{2+}]}{[Cu^{2+}]_2}\right]$$

$$= \frac{2.303RT}{2F}\log\left(\frac{[Zn^{2+}]}{[Cu^{2+}]_1}\times\frac{[Cu^{2+}]_2}{[Zn^{2+}]}\right)$$

$$= \frac{2.303RT}{2F}\log\left(\frac{[Cu^{2+}]_2}{[Cu^{2+}]_1}\right)$$

Given that $E_2 - E_1 = 0.03$ V and $[Cu^{2+}]$ in the second cell is 0.5 M. Substituting, we get

$$0.03 = \frac{2.303\times 8.314\times 300}{2\times 96500}\log\left(\frac{0.5}{[Cu^{2+}]_1}\right)$$

or $$0.03 = 0.03\log\left(\frac{0.5}{[Cu^{2+}]_1}\right)$$

$$1 = \log\left(\frac{0.5}{[Cu^{2+}]_1}\right) \Rightarrow \frac{0.5}{[Cu^{2+}]_1} = 10$$

or $$[Cu^{2+}]_1 = 0.05\text{ M}$$

Solved Example 11-29

(a) Calculate $\Delta_r G^\circ$ of the following reaction

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$$

Given that

$\Delta G^o_{f(AgCl)} = -109\text{ kJ mol}^{-1}$, $\Delta G^o_{f(Cl^-)} = -129\text{ kJ mol}^{-1}$

and $\Delta G^o_{f(Ag^+)} = 77\text{ kJ mol}^{-1}$.

Represent the above reaction in form of a cell. Calculate E^o_{cell} and find $\log_{10}K_{sp}$ of AgCl.

(b) 6.539×10^{-2} g of metallic Zn (65.39 amu) was added to 100 mL of saturated solution of AgCl, calculate $\log_{10}\dfrac{[Zn^{2+}]}{[Ag^+]^2}$. Given that:

$$Ag^+(aq) + e^- \rightarrow Ag(s) \qquad E^o_{cell} = 0.80\text{ V}$$
$$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s) \qquad E^o_{cell} = -0.76\text{ V}$$

Also find how many moles of Ag will be formed.

(IIT-JEE 2005)

Solution

(a) The cell reactions are

$$Ag^+(aq) + \tfrac{1}{2}Cl^-(aq) \rightarrow AgCl(s)$$
$$Ag(s) \rightarrow Ag^+(aq) + e^-$$
$$\tfrac{1}{2}Cl_2(g) + e^- \rightarrow Cl^-(aq)$$

The net reaction is $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$.

The cell representation is $Ag|Ag^+|AgCl||\,Cl^-|Cl_2, Pt$.

$\Delta G^o = -109 - (-129 + 77) = -109 + 129 - 77$

$= -57 = -1\times F\times E^o$

Therefore, $E^o_{cell} = \dfrac{57000}{96500} = 0.59$ V

Now, $\Delta G^o = -2.303\ RT\log K$. So, we have

$$\log K = \frac{57\times 1000}{2.303\times 8.314\times 298} = 9.98 \approx 10 \Rightarrow K = 10^{10}$$

But, $K_{sp} = 1/K$, so $K_{sp} = 10^{-10} \Rightarrow \log K_{sp} = -10$.

(b) The solubility, *S* is calculated as follows.

$K_{sp} = S^2 \Rightarrow S = (10^{-10})^{1/2} = 10^{-5}$ mol L^{-1}

Adding the reactions, we get

$$2\text{Ag}^+(\text{aq}) + 2e^- \rightarrow 2\text{Ag}(\text{s}); \quad E^o_{\text{cell}} = 0.80 \text{ V}$$
$$\text{Zn}(\text{s}) \rightarrow \text{Zn}^{2+}(\text{aq}) + 2e^-; \quad E^o_{\text{cell}} = +0.76 \text{ V}$$

we get

$$2\text{Ag}^+(\text{aq}) + \text{Zn}^{2+}(\text{aq}) \rightarrow 2\text{Ag}(\text{s}) + \text{Zn}(\text{s})$$
$$E^o_{\text{cell}} = 0.80 + 0.76 = 1.56 \text{ V}$$

At equilibrium, $E_{\text{cell}} = 0$

Therefore, $E^o_{\text{cell}} = \dfrac{0.0591}{2}\log\dfrac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2}$

$$1.56 \times \frac{2}{0.0591} = \log\frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2} \Rightarrow \log\frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2} = 52.8$$

Given that (6.539 × 10^{-2})/65.39 = 10^{-3} mol of Zn has been added. Now, 10^{-6} mol of Ag reacts with 10^{-3} mol of Zn. Therefore, this reaction will move in forward direction completely. Hence, moles of Ag formed will be 10^{-6} mol.

Solved Example 11-30

Find the solubility product of a saturated solution of Ag_2CrO_4 in water at 298 K if the emf of the cell

$$\text{Ag} \,|\, \text{Ag}^+(\text{saturated Ag}_2\text{CrO}_4 \text{ soln.}) \,||\, \text{Ag}^+(0.1 \text{ M}) \,|\, \text{Ag}$$

is 0.169 V at 298 K.

Solution

Applying Nernst equation, we get $E_{\text{cell}} = \dfrac{0.0591}{1}\log\dfrac{C_2}{C_1}$

where C_2 is the concentration of Ag^+ and C_1 is the concentration of Ag_2CrO_4. Hence,

$$0.164 = \frac{0.0591}{1}\log\frac{0.1}{C_1}$$

where $C_1 = 1.679 \times 10^{-4}$. This means concentration of $[Ag^+]$ in $Ag_2CrO_4 = 1.679 \times 10^{-4}$ M. According to the reaction

$$\text{Ag}_2\text{CrO}_4 \rightarrow 2\ \text{Ag}^+ + \text{CrO}_4^{2-}$$

we have $[Ag^+] = 1.679 \times 10^{-4}$ M, so

$$[\text{CrO}_4^{2-}] = \frac{[\text{Ag}^+]}{2} = \frac{1.679\ \times 10^{-4}}{2}$$

Therefore,

$$K_{sp} = [\text{Ag}^+]^2[\text{CrO}_4^{2-}] = (1.679 \times 10^{-4})^2 \times \left(\frac{1.679 \times 10^{-4}}{2}\right)$$
$$= 2.37 \times 10^{-12}$$

Solved Example 11-31

Calculate reduction potential at pOH = 14 for the Cu^{2+}/Cu. Given that $E^o_{Cu^{2+}/Cu} = 0.34$ V and $(K_{sp})_{Cu(OH)_2} = 1 \times 10^{-19}$.

Solution

Given that pOH = 14 ⇒ $-\log[OH^-] = 14 \Rightarrow [OH^-] = 10^{-14}$ M

Now,

$$[\text{Cu}^{2+}][\text{OH}^-]^2 = K_{sp} \Rightarrow [\text{Cu}^{2+}] = \frac{K_{sp}}{[\text{OH}^-]^2} = \frac{10^{-19}}{10^{-28}} = 10^9 \text{ M}$$

From the reaction $Cu^{2+} + 2e^- \rightarrow Cu$, we have

$$E_{\text{Cu}^{2+}/\text{Cu}} = E^o_{\text{Cu}^{2-}/\text{Cu}} - \frac{0.59}{2}\log\frac{1}{[\text{Cu}^{2+}]} = 0.34 - \frac{0.0591}{2}\log 10^9$$
$$= 0.34 - \frac{0.059 \times 19}{2} = 0.34 - 0.56 = -0.22 \text{ V}$$

Potentiometric Titrations

Potentiometric titrations involve measurement of electrode potential with help of titrations. There are three types of potentiometric titrations, which are discussed as follows.

Acid Base Titrations

Titration of HCl vs. NaOH solution is an example of acid-base titration. The potential in this case depends upon H^+ ion. As the titration proceeds (on addition of NaOH), $[H^+]$ decrease and pH of the solution increase. Therefore, E_{cell} also increases.

A reference electrode like SCE is taken to observe the change in E_{cell}.

$$\text{Pt, H}_2(1\text{atm})|\text{H}^+(\text{C}_1,\text{unknown})\|\text{KCl(saturated)}, \text{Hg}_2\text{Cl}_2(\text{s}), \text{Hg}$$

The titration curve is very steep near the equivalence point (Fig. 11.11).

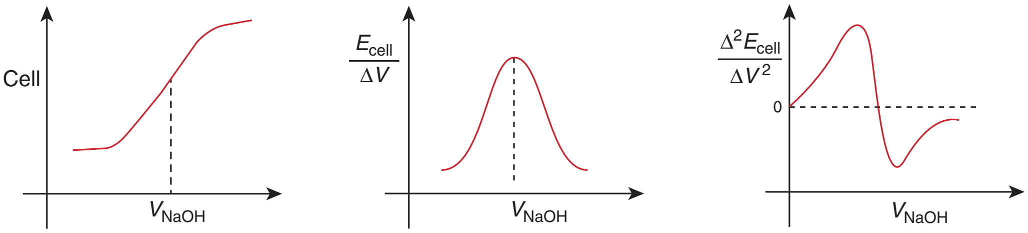


Figure 11.11 Acid-base titration of HCl vs. NaOH.

Here ΔV is the change in volume of titrant and V_{NaOH} is the volume of NaOH.

Solved Example 11-32

25 mL (0.1 M) HCl is titrated against standard (0.1 M) NaOH using hydrogen electrode as indicator electrode and SCE as reference electrode. Calculate E_{cell} at 25°C

(a) At the start of the titration.

(b) After adding 20 mL of NaOH.

(c) After adding 25 mL of NaOH.

(Given $E_{\text{SCE}} = 0.24\,\text{V}$.)

Solution

For the given cell

$$\text{Pt, H}_2(1\,\text{atm})|\text{H}^+\,(\text{unknown})\|\text{KCl(saturated)}|\text{Hg}_2\text{Cl}_2(\text{s}),\text{Hg}$$

$$\begin{aligned} E_{\text{cell}} &= E_{\text{RHS}} - E_{\text{LHS}} \\ &= E_{\text{SCE}} - E_{\text{H}^+/\text{H}_2} \\ &= 0.24 + 0.059\,\text{pH} \end{aligned}$$

(a) At the start

$$\text{pH} = -\log \text{H}^+ = -\log(0.1) = 1$$

$$E_{\text{cell}} = 0.24 + 0.059 = 0.299\,\text{V}$$

(b) After adding 20 mL of NaOH

$$[\text{H}^+] = \frac{(2.5-2)}{(20+25)} = 0.011$$

$$\text{pH} = -\log(0.11) = 1.95$$

$$E_{\text{cell}} = 0.24 + 0.059(1.95) = 0.355\,\text{V}$$

(c) $[\text{H}^+]$ is completely equal to $[\text{OH}^-]$

Therefore, pH = 7

$$E_{\text{cell}} = 0.24 + 0.059(7) = 0.653\,\text{V}$$

Redox Titrations

Similar to acid base titrations, we can understand redox titrations through the following example.

Solved Example 11-33

Calculate E_{cell} for a cell consisting of SCE and a platinum wire indicator electrode dipped in a titration vessel containing 25 mL (0.01 M) Fe^{2+} after addition of **(a)** 5 mL, **(b)** 25 mL and **(c)** 50 mL of 0.01 M Ce^{4+} solution. (SCE is attached to negative terminal of the voltmeter. Given: $E^{\circ}_{\text{Fe}^{3+}/\text{Fe}^{2+}} = -0.77$ V; $E^{\circ}_{\text{Ce}^{4+}/\text{Ce}^{3+}} = +1.61$ V; $E_{\text{SCE}} = -0.24\,\text{V}$.)

Solution

For the given cell

$$\text{Hg, HgCl}_2(\text{s}),\text{KCl}\|\text{Fe}^{2+},\text{Fe}^{3+}|\text{Pt}$$

At anode: $\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+} + e^-$

At cathode: $\text{Ce}^{4+} + e^- \rightleftharpoons \text{Ce}^{3+}$

Cell reaction: $\text{Ce}^{4+} + \text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+} + \text{Ce}^{3+}$

Before the equivalence point, E_{cell} is controlled by Fe^{2+} and Fe^{3+} concentrations and after the equivalence point it is controlled by Ce^{4+} and Ce^{3+} concentrations.

(a) After addition of 5 mL of 0.01 M Ce^{4+} solution, the final volume is 30 mL.

$$\begin{array}{cccc} \text{Fe}^{2+} & +\,\text{Ce}^{4+} & \rightleftharpoons\ \text{Fe}^{3+} & +\,\text{Ce}^{3+} \\ 25\times 0.01 & 5\times 0.01 & & \\ 0.025-0.05 = 0.20\ \text{mmol} & 0 & 0.05\ \text{mmol} & \end{array}$$

Because $[\text{Fe}^{2+}] = \dfrac{0.20}{25+5}$, $[\text{Fe}^{3+}] = \dfrac{0.05}{25+5}$. Therefore,

$$E_{\text{cell}} = \left(0.77 + \frac{0.059}{1}\log\frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}\right) - 0.24$$

$$= \left(0.77 + 0.059\log\frac{(0.05/30)}{(0.2/30)}\right) - 0.24$$

$$= 0.494\ \text{V}$$

(b) If 25 mL of 0.01 M Ce^{4+} solution is added, then

$$m_{\text{eq}} \text{ of } \text{Fe}^{2+} = m_{\text{eq}} \text{ of } \text{Ce}^{4+}$$

Therefore, equivalence point is reached

$$[\text{Fe}^{2+}] = [\text{Ce}^{4+}] \text{ and } [\text{Fe}^{3+}] = [\text{Co}^{3+}]$$

$$(E_{\text{cell,eq}})_{\text{RHS}} = \left(0.77 + 0.059\log\frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}\right)$$

$$(E_{\text{cell,eq}})_{\text{RHS}} = \left(1.61 + 0.059\log\frac{[\text{Ce}^{4+}]}{[\text{Ce}^{3+}]}\right)$$

$$2(E_{\text{cell,eq}})_{\text{RHS}} = 0.77 + 1.61 + 0059\log\frac{[\text{Fe}^{3+}]\,[\text{Ce}^{4+}]}{[\text{Fe}^{2+}]\,[\text{Ce}^{3+}]}$$

Therefore,

$$(E_{\text{cell,eq}})_{\text{RHS}} = \frac{(0.77+1.61)}{2} = 1.91\ \text{V}$$

$$E_{\text{cell}} = 1.19 - 0.24 = 0.95\ \text{V}$$

(c) After addition of 50 mL of 0.01 M Ce^{4+} solution

$$\left[(\text{Ce}^{4+})_{\text{left}}\right] = \frac{[50\times 0.01 - 25\times 0.01]}{(25+50)} = \frac{0.25}{75}$$

$$\left[(\text{Ce}^{4+})_{\text{formed}}\right] = \frac{25\times 0.01}{(25+50)} = \frac{0.25}{75}$$

$$E_{\text{cell}} = \left[1.61 + 0.059\log\frac{[\text{Ce}^{4+}]}{[\text{Ce}^{3+}]}\right] - 0.24$$

$$= 1.37$$

Precipitation Titrations

We standardize AgNO_3 solution using the Ag electrode as the indicator electrode. We calculate the potential of Ag electrode by connecting it to a SCE. This solution is titrated against KCl and as the reaction progresses, Ag^+ ions are precipitated as AgCl.

$$\text{AgNO}_3 + \text{KCl} \rightarrow \text{AgCl}\downarrow + \text{KNO}_3$$

As $[\text{Ag}^+]$ concentration decreases, potential of Ag^+/Ag electrode is given by

$$E = E^{\circ}_{\text{electrode}} - \frac{0.0591}{1}\log\frac{1}{[\text{Ag}^+]}$$

The potentiometric curve is similar to that obtained in acid base titration, with the maximum change in electrode potential at the end point.

11.9 | ELECTROLYTIC CELLS AND ELECTROLYSIS

The cells discussed so far have one thing in common: They all use a spontaneous chemical reaction to produce an electric current in an external circuit. But they are not the only kind of cell. It is also possible to construct a cell that does work on a chemical system by applying a potential to the cell that causes an electric current to flow through the cell. These cells are called **electrolytic cells**. Electrolysis is used to drive an oxidation–reduction reaction (distinguishing features of galvanic and electrolytic cells are given in Table 11.2) in the direction in which it does not occur spontaneously.

For example, a simple electrolytic cell may be constructed by dipping two copper strips in a solution of copper salt. Such a cell is used in purification of impure copper obtained from its ore. The impure copper (containing zinc, iron, silver and gold as impurities) is used as the anode in an electrolytic cell that contains a solution of copper sulphate and sulphuric acid as the electrolyte. The cathode is a thin sheet of very pure copper. When the cell is operated at the correct voltage, only copper and impurities more easily oxidized than copper (iron and zinc) dissolve at the anode. The less active metals simply fall off the electrode and settle to the bottom of the container. At the cathode, copper ions are reduced, but the zinc ions and iron ions remain in solution because they are more difficult to reduce than copper. Gradually, the impure copper anode dissolves and the pure copper cathode grows larger.

Table 11.2 Distinguishing features of electrolytic and electrochemical (galvanic) cells

Electrochemical cell (Galvanic cell)	Electrolytic cell
Converts chemical energy to electrical energy.	Converts electrical energy to chemical energy.
Spontaneous redox reaction takes place leading to generation of electrical energy.	Redox reaction is non-spontaneous and electrical energy is required to start the reaction.
The two electrodes are placed in separates containers connected by a salt bridge.	The two electrodes are placed in the same container containing molten solution of electrolyte.
The source of electrons are the species undergoing redox reaction.	Source of electrons is the external battery.

Faraday's Laws of Electrolysis

If a voltage larger than the cell voltage of galvanic cell is applied in opposition to the cell causing electron flow in the reverse direction), then the chemical reaction can be made to run in the opposite (non-spontaneous) direction. This property is used to charge a battery or in some cases to prepare a pure reactive element from its oxide or halide.

The amount (moles) of material reacted or produced depends on the balanced chemical reaction and the mole of electrons transferred. The mole of electrons transferred can be calculated from the current (I) and the time (t) the current flows. The rate (I) at which a current flows is measured in amperes (A).

$$1\ \text{A} = 1\ \text{C s}^{-1}$$

where C is coulomb. The total amount of charge passing through a circuit can be determined by multiplying current flow (I) measured in amps by time (t). The moles of electrons passed through the circuit (n) can be determined by dividing the amount of charge by the Faraday's constant (F), which is the charge of a mole of electrons.

$$n = \frac{It}{F} \tag{11.22}$$

where n = moles of electrons, I = current (C s^{-1}), t = time (s) and F = 96500 (C mol^{-1}).

First Law

It states that the weight of a substance liberated at an electrode during electrolysis is directly proportional to the charge passed through the electrolytes.

$$w \propto Q \Rightarrow w \propto It$$

or
$$w = ZQ = ZIt \tag{11.23}$$

where Z is the electrochemical equivalent of that substance. Now, if I = 1 A and t = 1 s (or Q = 1 C), then $w = Z$, that is, Z can be defined as the weight of a substance deposited or liberated when 1 C of charge is utilized by the solution. From Eq. (11.23), we have

$$w = \frac{M}{n \times F} \times I \times t \quad \left(\text{using } Z = \frac{\text{molar mass}}{n \times \text{Faraday}}\right)$$

Now, 1 mol of *electrons* = 1 equivalent of *electrons* = 96,500 C = 1 F.

Therefore,
$$\frac{w}{E} = \text{Number of equivalents} = \frac{It}{96500} \tag{11.24}$$

where E is the number of equivalents $= \dfrac{M}{n\text{-factor}}$

Note: Current efficiency is the ratio of the observed mass of products at the electrode to the expected mass of products.

Thickness of the Deposited Layer

The first law can be used to determine the **thickness of the coated layer in electroplating** (discussed later).

Let the dimension of the metal sheet to be coated be l cm × b cm and the thickness of the metal coating be h cm. Then,

$$\text{Volume of the coated layer} = (l \times b \times h\ \text{cm}^3)$$

$$\text{Mass of metal deposited} = \text{Volume} \times \text{density} = (l \times b \times h\ \text{cm}^3) \times \rho\ \text{g}$$

Then from the first law,

$$(l \times b \times h\ \text{cm}^3) \times \rho\ \text{g} = \frac{I \times t \times E}{96500} \tag{11.25}$$

If the length and breadth of the metal plate is known, we can determine the thickness of layer to be formed by a given amount of current passed for a given interval.

Note: Sometimes radius (R) of metal atom to be deposited is given instead of density. In such cases, the density of the metal is determined by the relation

$$\text{Density} = \frac{\text{Mass of single atom}}{\text{Volume of single atom}} = \frac{\text{Molecular weight/Avogadro's number}}{(4/3)\pi R^3} \tag{11.26}$$

Solved Example 11-34

A current of 1.7 A is passed through 300 mL of 0.16 M solution of $ZnSO_4$ for 230 s with a current efficiency of 90%. Find the final molarity of Zn^{2+} assuming volume is constant.

Solution

Equivalent of Zn^{2+} lost is

$$\frac{It}{96500} = \frac{1.7 \times 90 \times 230}{100 \times 96500} = 6.646 \times 10^{-3}$$

Therefore, milliequiv. of Zn^{2+} lost = 6.646 milliequiv.
Initial milliequiv. of $Zn^{2+} = 300 \times 0.16 \times 2 = 96$ milliequiv.
The milliequiv. left = 96 – 3.646 = 92.354 milliequiv.
Therefore, the final molarity of

$$Zn^{2+} = \frac{92.354}{2 \times 300} = 0.154\ \text{M}$$

Solved Example 11-35

A current of one ampere is flowing through a wire. Calculate the number of electrons flowing through the cross-section of the wire per second.

Solution

We have $Q = I \times t = 1 \times 1 = 1$ C. As 1 F (96,500 C) is equivalent to 1 mol (i.e., 6.023×10^{23} electrons)

$$\text{So, } 1\ \text{C} = \frac{6.023 \times 10^{23}}{96500} = 6.24 \times 10^{18}\ \text{electrons}$$

Solved Example 11-36

For how long a current of 3 A has to be passed through a solution of $AgNO_3$ to coat a metal surface of 80 cm^2 area with 0.005 mm thick layers? Density of silver is 10.5 g cm^{-3} and atomic weight of Ag is 108 g mol^{-1}.

Solution

Suppose the coating has to be done only on one side of the surface, then volume of Ag required for coating is

$$\frac{80\times 0.005}{10}=0.04\ \text{cm}^3$$

Amount of silver = 10.5 × 0.04 = 0.42 g and

moles of silver $=\frac{0.42}{108}=0.00389$ mol

From the reaction $Ag^+(aq)+e^-\rightarrow Ag(s)$, the number of moles of electrons = 0.00389. The amount of charge passed is

$$Q=0.00389\times 96500=375.385\ \text{C}$$

Therefore, time, $t=\frac{375.385}{3}=125.12$ s.

Solved Example 11-37

H_2O_2 can be prepared by successive reactions.

$$2NH_4HSO_4\rightarrow H_2+(NH_4)_2S_2O_8$$

$$(NH_4)_2S_2O_8+2H_2O\rightarrow 2NH_4HSO_4+H_2O_2$$

The first is an electrolytic reaction and the second a steam distillation. What current needs to be passed in the first reaction to produce enough intermediate to yield 10 g of pure H_2O_2 per hour? Assume 50% current efficiency.

Solution

We find that 100 g of pure H_2O_2 will contain 100/34 mol of H_2O_2
Moles of $(NH_4)_2S_2O_8$ that would have reacted = 100/34 mol
Moles of $(NH_4)_2S_2O_8$ that need to be formed by the first reaction = 100/34 mol

Moles of NH_4HSO_4 that needs to react $=\frac{100}{34}\times 2=\frac{100}{17}$

When 1 mol of NH_4HSO_4 gets converted into $(NH_4)_2S_2O_8$, 2 mol of electrons would be liberated. This is because in NH_4HSO_4 all the oxygen atoms have an oxidation state of –2. In $(NH_4)_2S_2O_8$, two oxygen atoms are linked to each other (by peroxide linkage) because of which their oxidation state becomes –1. Therefore, two oxygen atoms have been oxidized from –2 to –1.

Moles of electrons given by

$$\frac{100}{17}\ \text{of}\ NH_4HSO_4=\frac{100}{17}\ \text{mol}$$

$$\text{Charge}=\frac{100}{17}\times 96500=577647.05\ \text{C}$$

$$\text{The current } I=\frac{577647.05}{60\times 60}\times\frac{100}{50}=315.36\ \text{A}$$

Solved Example 11-38

Perdisulphuric acid ($H_2S_2O_8$) can be prepared by electrolytic oxidation of H_2SO_4 with half-cell reaction $2H_2SO_4\rightarrow H_2S_2O_8+2H^++2e^-$. Here O_2 and H_2 are obtained as byproducts in the whole process. In such an electrolysis 0.87 g of H_2 and 3.36 g of O_2 were generated at STP. Calculate the total quantity of current passed through the solution to carry out electrolysis. Also report the weight of $H_2S_2O_8$ formed.

Solution

The reactions involved are
At the anode:

$$2H_2SO_4(aq)\rightarrow H_2S_2O_8(s)+2H^+(aq)+2e^-$$
$$2H_2O(l)\rightarrow O_2(g)+4H^+(aq)+4e^-$$

At cathode: $2H^+(aq)+2e^-\rightarrow H_2(g)$

In the electrolysis of H_2SO_4, initially H_2SO_4 oxidizes at anode until all of it gets converted into $H_2S_2O_8$, after which O_2 is evolved by the electrolysis of H_2O. Simultaneously, H_2 is evolved at cathode and continues till the entire process.
The total charge required to produce 0.87 g of H_2 is

$$\frac{2\times 96500\times 0.87}{2}=83955\ \text{C}$$

The quantity of charge required to produce 3.36 g of O_2 is

$$\frac{4\times 96500\times 3.36}{32}=40530\ \text{C}$$

Hence, the quantity of charge used up in the formation of $H_2S_2O_8=83955-40530=43425$ C

and the amount of $H_2S_2O_8$ formed $=\frac{194\times 43425}{2\times 96500}=43.65$ g

Solved Example 11-39

A current of 40 μA is passed through a solution of $AgNO_3$ for 32 min using Pt electrodes. A uniform single atom thick layer of Ag is deposited covering 43% cathode surface. What is the total surface area of cathode, if each Ag atom covers 5.4×10^{-16} cm^2?

Solution

The total amount of charge passed = $(4 \times 10^{-6} \times 32 \times 60)$ = 0.0768 C

$$\mathrm{Ag^+(aq)} + e^- \rightarrow \mathrm{Ag(s)}$$

So, the amount of Ag deposited at cathode surface is

$$\frac{108 \times 0.0768}{96500} = 8.6 \times 10^{-5}\ \mathrm{g}$$

Now, the total number of Ag atoms deposited is

$$\frac{8.6 \times 10^{-6}}{108} \times 6.023 \times 10^{23} = 4.8 \times 10^{17}$$

So, the surface area of cathode which is covered by Ag atoms = $4.8 \times 10^{17} \times 5.4 \times 10^{-16} = 259.2$ cm^2

$$\text{Hence, the total surface area} = \frac{259.2 \times 100}{43} = 602.8\ \mathrm{cm^2}$$

Second Law

The second law states that if the same quantity of electricity is passed in two different solutions, then the amount of substance deposited or dissolved are proportional to their chemical equivalent weights.

From Eq. (11.34), we have

$$\frac{w}{E} = \frac{It}{96500}$$

If It = constant, then w/E is constant. So,

$$\frac{w_1}{E_1} = \frac{w_2}{E_2} \qquad (11.27)$$

From the above equation, we have

$$\frac{\text{Wt. of M}_1\text{ deposited}}{\text{Wt. of M}_2\text{ deposited}} = \frac{\text{Eq. wt. of M}_1}{\text{Eq. wt. of M}_2} \qquad (11.28)$$

Solved Example 11-40

Cadmium amalgam is obtained by the electrolysis of a solution of cadmium chloride using a mercury cathode. For how long the process of electrolysis should be carried out to prepare a 12% (by wt.) of cadmium amalgam using 44 g of mercury and a current of 5 A? (Atomic weight of Cd = 112 u).

Solution

Since 88 g Hg has 12 g Cd, so 44 g Hg requires

$$\frac{12 \times 44}{88} = 6\ \mathrm{g\ Cd}$$

Now, 56 g Cd is required to deposit 96500 C charges
So, 6 g Cd is required to deposit

$$\frac{96500}{56} \times 6\ \mathrm{C} = 10339.286\ \mathrm{C}$$

Therefore, the time required is

$$t = \frac{Q}{I} = \frac{10339.286}{5} = 20678.57\ \mathrm{s} = 34.4\ \mathrm{min}$$

Solved Example 11-41

The same quantity of electricity that liberates 4.316 g of silver from $AgNO_3$ solution was passed through a solution of gold salt. If the atomic weight of gold be 197 u and its valency in the above-mentioned salt be 3, calculated the weight of gold deposited at the cathode and the quantity of electricity passed.

Solution

We know that

$$\frac{w_{\text{Ag}}}{w_{\text{Au}}} = \frac{E_{\text{Ag}}}{E_{\text{Au}}}$$

Substituting values, we get

$$\frac{4.37}{w_{\text{Au}}} = \frac{107.9}{65.6} \Rightarrow w_{\text{Au}} = 2.62\ \text{g}$$

Therefore, $$Q = \frac{96500 \times 2.62}{65.6} = 3854.1\ \text{C}$$

Solved Example 11-42

Calculate the mass of silver metal that will form at the cathode when a 10 A current is passed through the electrolysis cell for a period of 5 min.

Solution

We start by calculating the amount of electric charge that flows through the cell.

$$10.0\ \text{A} \times 5.00\ \text{min} \times \frac{60\ \text{s}}{1\ \text{min}} \times \frac{1\ \text{C}}{1\ \text{A} \cdot \text{s}} = 3.00 \times 10^3\ \text{C}$$

The number of moles of electrons transferred when 3×10^3 C of electric charge flows through the cell can be calculated as follows.

$$3.00 \times 10^3\ \text{C} \times \frac{1\ \text{mol}}{96,485\ \text{C}} = 3.11 \times 10^{-2}\ \text{mol}$$

According to the balanced equation for the half-reaction that occurs at the cathode of the cell, we get 1 mol of silver for every mole of electrons. Thus, we get 3.11×10^{-2} mol or 3.35 g of silver in 5 min.

$$3.11 \times 10^{-2}\ \text{mol Ag} \times \frac{107.9\ \text{g Ag}}{1\ \text{mol Ag}} = 3.35\ \text{g Ag}$$

Solved Example 11-43

If 0.3605 g of a metal is deposited on the electrode by passing 1.2 A current for 15 min through its salt, what will be its valency? (Atomic weight of the metal is 96u)

Solution

We know that $Q = w/E$ and $Q = I \times t$. So,

$$\frac{w}{E} = \frac{I \times t}{96500} \Rightarrow \frac{0.3605}{96/n} = \frac{1.2 \times 15 \times 60}{96500}$$

or $0.3605 \times n \times 96500 = 1.2 \times 15 \times 60 \times 96$

Therefore, $$n = \frac{1.2 \times 15 \times 60 \times 96}{0.3605 \times 96500} = 2.9803 \cong 3$$

Products Formed in Electrolysis

A number of factors determine the products formed during electrolysis and these are discussed as follows.

1. **Nature of electrolyte:** Different products are obtained on electrolysis depending upon if the electrolyte is present in molten or aqueous state. For example, in the electrolysis of molten NaCl, the products formed are sodium metal and chlorine gas. The reactions at the cathode and the anode can be depicted as

$$\text{Na}^+(\text{aq}) + e^- \rightarrow \text{Na(l)}$$

$$2\text{Cl}^-(\text{aq}) \rightarrow \text{Cl}_2(\text{g}) + 2e^-$$

However, when electrolysis of aqueous solution of NaCl is carried out, the products obtained are NaOH, Cl_2 and H_2. This is because H^+ and OH^- ions obtained from electrolysis of water (solvent) molecules are also present along with Na^+ and Cl^- ions.

The two competing reactions at the cathode are:

$$\text{Na}^+(\text{aq}) + e^- \rightarrow \text{Na(s)}; \quad E^{\circ}_{\text{cell}} = -2.71\ \text{V}$$

$$\text{H}^+(\text{aq}) + e^- \rightarrow \tfrac{1}{2}\text{H}_2(\text{g}); \quad E^{\circ}_{\text{cell}} = 0.0\ \text{V}$$

The reaction with higher value of E° is preferred, and therefore, the reaction at the cathode during electrolysis is

$$\mathrm{H^+(aq)} + e^- \rightarrow \tfrac{1}{2}\,\mathrm{H_2(aq)}$$

but H^+ (aq) is produced by the dissociation of H_2O, that is,

$$\mathrm{H_2O(l)} \rightarrow \mathrm{H^+(aq)} + \mathrm{OH^-(aq)}$$

Therefore, the net reaction at the cathode may be written as

$$\mathrm{H_2O\,(l)} + e^- \rightarrow \tfrac{1}{2}\,\mathrm{H_2(g)} + \mathrm{OH^-(aq)}$$

At the anode the following oxidation reactions are possible:

$$\mathrm{Cl^-(aq)} \rightarrow \tfrac{1}{2}\mathrm{Cl_2(g)} + e^-; \quad E^\circ_{\mathrm{cell}} = 1.36\ \mathrm{V}$$

$$\mathrm{2H_2O(l)} \rightarrow \mathrm{O_2(g)} + \mathrm{4H^+(aq)} + 4e^-; \quad E^\circ_{\mathrm{cell}} = 1.23\ \mathrm{V}$$

The reaction at anode with lower value of E° is preferred and therefore, water should be oxidized in preference to Cl^- (aq). However, it is observed that oxidation of chloride ions takes place in preference over oxidation of water. Thus, the reactions taking place may be summarized as:

$$\mathrm{NaCl(aq)} \xrightarrow{\mathrm{H_2O}} \mathrm{Na^+(aq)} + \mathrm{Cl^-(aq)}$$

At the cathode: $\mathrm{H_2O(l)} + e^- \rightarrow \tfrac{1}{2}\mathrm{H_2(g)} + \mathrm{OH^-(aq)}$

At the anode: $\mathrm{Cl^-(aq)} \rightarrow \tfrac{1}{2}\mathrm{Cl_2(g)} + e^-$

Overall cell reaction: $\mathrm{NaCl(aq)} + \mathrm{H_2O(l)} \rightarrow \mathrm{Na^+(aq)} + \mathrm{OH^-(aq)} + \tfrac{1}{2}\mathrm{H_2(g)} + \tfrac{1}{2}\mathrm{Cl_2(g)}$

Although chloride ion lies below hydroxide ion in the electrochemical series, still chloride is oxidized in preference to hydroxide ion. This is because of **overpotential** or **overvoltage**. Overpotential is the extra potential required to start a reaction. Oxidation of hydroxide ion to give O_2 is very slow kinetically. Thus effectively, we get Cl_2 at anode and OH^- remains in the solution.

2. **Nature of electrodes:** The products formed on electrolysis also depend on the electrode being inert or reactive. If the electrodes are made of inert materials such as platinum, they function only as source or sink of electrons. However, reactive electrodes, such as the pure copper cathode used in electrochemical reduction of copper, participate in the reactions and affect the products of electrolysis. For example, if Hg electrodes are used during the electrolysis of aq. NaCl, the products we get at anode and cathode are different.

At anode: Cl^- oxidizes to give Cl_2.
At cathode: Hg selectively increases the overvoltage of H_2O giving H_2. Thus we get the reduction of Na^+ to give Na at cathode.
This Na combines with Hg to Na–Hg amalgam which can be easily separated.
To obtain Na, this amalgam can be heated.
To obtain NaOH solution, water can be added to this amalgam.

3. **Standard electrode potentials of oxidizing and reducing species:** Consider the electrolysis of an aqueous solution of copper (II) bromide, $CuBr_2$, let us examine the possible electrode half-reactions and their respective standard reduction potentials.

At the cathode, possible reactions are the reduction of copper ion and the reduction of water. From Table 11.1

$$\mathrm{Cu^{2+}(aq)} + 2e^- \rightarrow \mathrm{Cu(s)}; \quad E^\circ_{\mathrm{Cu^{2+}}} = +0.34\ \mathrm{V}$$

$$\mathrm{2H_2O(l)} + 2e^- \rightarrow \mathrm{H_2(g)} + \mathrm{2OH^-(aq)}; \quad E^\circ_{\mathrm{H_2O}} = -0.83\ \mathrm{V}$$

The much more positive standard reduction potential for Cu^{2+} tells us that Cu^{2+} will be reduced at the cathode. At the anode, possible reactions are the oxidation of Br^- and the oxidation of water. The half-reactions are

$$2Br^-(aq) \rightarrow Br_2(aq) + 2e^-$$

$$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$$

Based on Table 11.1,

$$2Br_2(aq) + 2e^- \rightarrow 2Br^-(aq); \quad E^o_{Br_2} = +1.07\ V$$

$$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l); \quad E^o_{O_2} = +1.23\ V$$

The data tell us that O_2 is more easily reduced than Br_2, which means that Br^- is more easily oxidized than H_2O.

Therefore, we expect that Br^- will be oxidized at the anode. In the actual electrolysis reaction, the products predicted on the basis of standard electrode potential values are obtained.

At the anode: $2Br^-(aq) \rightarrow Br_2(aq) + 2e^-$

At the cathode: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Overall cell reaction: $Cu^{2+}(aq) + 2Br^-(aq) \xrightarrow{\text{Electrolysis}} Cu(s) + Br_2(aq)$

4. **Concentration of solution used:** To take into account the effect of variation in concentration, standard electrode potentials are replaced with the electrode potentials obtained using the Nernst equation. For example, in the electrolysis of sulphuric acid, the two reactions possible at the anode are as follows:

$$2SO_4^{2-}(aq) \rightarrow S_2O_8^{2-}(aq) + 2e^-; \quad E^o_{cell} = +1.96\ V$$

$$2H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^-; \quad E^o_{cell} = +1.23\ V$$

At dilute concentrations, oxygen is formed at the anode and at high concentrations of acid, $S_2O_8^{2-}$ is obtained.

Transport (Transference) Number

It is an established fact that during electrolysis, the current is carried by both anions and cations. The fraction of the total current carried by the cation or anion is termed as transport number. Therefore, the current carried by the cation is

or

$$t_+ = \frac{\text{Current Carried by the cations}}{\text{Total current carried by both the ions}} \quad (11.29)$$

where t_+ is the transport number of the cation.

Similarly,

$$t_- = \frac{\text{Current Carried by the anions}}{\text{Total current carried by both the ions}} \quad (11.30)$$

where t_- is the transport number of the anion. Now, adding Eqs. (11.29) and (11.30), we get

$$t_+ + t_- = 1 \quad (11.31)$$

The current carried by an ion depends on the charge, speed and molal concentration of the ion. Therefore,

$$t_+ \propto Q_+ m_+ v_+ \quad \text{and} \quad t_- \propto Q_- m_- v_-$$

For an electrolyte, $m_+Q_+ = m_-Q_-$, because the solution is electrically neutral, therefore

$$\begin{aligned} t_+ &= \frac{v_+}{(v_+ + v_-)} \\ t_- &= \frac{v_-}{(v_+ + v_-)} \end{aligned} \tag{11.32}$$

The speeds of the ions are proportional to molar conductance, that is,

$$\frac{t_+}{t_-} = \frac{v_+}{v_-} = \frac{\lambda_+}{\lambda_-} \tag{11.33}$$

Ionic Mobility

Ionic mobility is defined as the distance travelled by an ion per second under a potential gradient of 1 volt per meter.

$$\text{Ionic mobility} = \frac{\text{Ionic velocity}}{\text{Potential gradient}} = \frac{V}{\mathrm{d}V/\mathrm{d}t} = \mathrm{m^2\,V^{-1}s^{-1}} \tag{11.34}$$

Solved Example 11-44

A decinormal solution of $AgNO_3$ was electrolyzed between Pt electrodes. After passing a small current for two hours, concentration of anodic solution reduced to 0.0005124 equiv. The weight of Cu deposited was 0.03879 g. Calculate the transport numbers of Ag^+ and NO_3^- in $AgNO_3$ solution.

Solution

Given that decrease in concentration = 0.0005124 equiv. and amount of Cu deposited = 0.03879 g. Therefore,

$$\text{equivalent of Cu deposited} = \frac{0.03879}{31.9} = 0.001216 \text{ equiv.}$$

Then transport number of Ag^+ =

$$t_{Ag^+} = \frac{\text{Equiv. of } Ag^+ \text{ lost}}{\text{Equiv. of } Cu^{2+} \text{ deposited}} = \frac{0.0005124}{0.001216} = 0.4214$$

$$\text{Now, } t_{Ag^+} + t_{NO_3^-} = 1 \Rightarrow t_{NO_3^-} = 1 - 0.4214 = 0.5786$$

Solved Example 11-45

A student set up an electrolysis apparatus and passed a current of 1.22 A through a 3 M H_2SO_4 solution for 30.0 min. The H_2 formed at the cathode was collected and found to have a volume, over water at 27 °C, of 288 mL at a total pressure of 767 torr. Use the data to calculate the charge on the electron, expressed in coulombs. Given that vapour pressure of water at 27 °C is 26.7 torr.

Solution

Our strategy will be thus:

Step 1: Pressure H_2 (wet) → partial pressure H_2 → mol H_2 → number of e^- used

The total pressure of wet hydrogen is 767 torr, but some of this is provided by water vapor. Given that the vapor pressure of water is 26.7 torr at 27°C. Therefore, pressure solely due to hydrogen gas (the partial pressure of hydrogen gas) is

$$\begin{aligned} p_{H_2} &= 767 - 26.7 = 740 \text{ torr} \\ &= 740 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.974 \text{ atm} \end{aligned}$$

Using the ideal gas law, $pV = nRT$, we get

$$(0.974 \text{ atm})(0.288 \text{ L}) = n \times (0.0821 \text{ L atm mol}^{-1}\text{K}^{-1}) \times (27 + 273 \text{ K})$$

Solving, we get n = 0.0114 mol H_2. According to the electrolysis equation $2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$, 2 mol of electrons are required per mol of H_2 gas formed. Therefore,

$$\text{Number of electrons} = 0.0114 \text{ mol } H_2 \times \left(\frac{2\text{ mol}}{1\text{ mol } H_2}\right)$$
$$\times 6.022\times10^{23}\ \text{electrons mol}^{-1}$$
$$= 1.37\times10^{22}\ \text{electrons}$$

Step 2: Find total charge used = (current) × (time) = (1.22 A) × (1800 s) = 2200 C

Step 3: The charge per electron can be arrived at by

$$\text{Charge per } e^- = \frac{\text{Total charge}}{\text{Total number of } e^- \text{used}} = \frac{\text{Step 1}}{\text{Step 2}}$$

Substituting, we get

$$\text{Charge per electron} = \frac{2200\text{ C}}{1.37\times10^{22}\ \text{electrons}}$$
$$= 1.61\times10^{-19}\ \text{C per electron}$$

(This is a very good estimate; the accepted value is 1.60×10^{-19} C.)

Solved Example 11-46

Suppose that a galvanic cell were set up having the net cell reaction

$$Zn(s) + 2Ag^+(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s)$$

The Ag^+ and Zn^{2+} concentrations in their respective half-cells initially are 1.00 M, and each half-cell contains 100 mL of electrolyte solution. If this cell delivers current at a constant rate of 0.10 A, what will the cell potential be after 15.00 h?

Solution

The initial numbers of moles of Ag^+ and Zn^{2+} are: 1.00 mol L^{-1} × 0.100 L = 0.100 mol. The number of coulombs (A × s) that have been employed is

$$0.10\text{ C s}^{-1} \times 15.00\text{ h} \times \frac{3600\text{ s}}{1\text{ h}} = 5.4\times10^3\text{ C}$$

The number of moles of electrons is

$$\frac{5.4\times10^3\text{ C}}{96500\text{ C mol}^{-1}} = 5.6\times10^{-2}\text{ mol electrons.}$$

For Ag^+, there is 1 mol per mole of electrons, and for Zn^{2+}, there are two moles of electrons per mol of Zn. This means that the number of moles of the two ions that have been consumed or formed is given by

5.6×10^{-2} mol e^- × (1 mol Ag^+/1 mol e^-) = 5.6×10^{-2} mol Ag^+ reacted.

5.6×10^{-2} mol e^- × (1 mol Zn^{2+}/2 mol e^-) = 2.8×10^{-2} mol Zn^{2+} formed

The number of moles of Ag^+ that remain is

$$0.100 - 0.056 = 0.044\text{ mol of } Ag^+$$

The final concentration of silver ion is

$$[Ag^+] = \frac{0.044\text{ mol}}{0.100\text{ L}} = 0.44\text{ M}$$

The number of moles of Zn^{2+} that are present is

$$0.100 + 0.028 = 0.128\text{ mol } Zn^{2+}$$

The final concentration of zinc ion is

$$[Zn^{2+}] = \frac{0.128\text{ mol}}{0.100\text{ L}} = 1.28\text{ M}$$

The standard cell potential should be

$$E^\circ_{\text{cell}} = E^\circ_{\text{reduction}} - E^\circ_{\text{oxidation}} = 0.80 - (-0.76) = 1.56\text{ V}$$

We now apply the Nernst equation

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592}{2}\log\frac{1.28}{(0.44)^2} = 1.56 - 0.024 = 1.54\text{ V}$$

11.10 | APPLICATIONS OF ELECTROLYTIC PROCESS

Corrosion and its Prevention

Corrosion can be defined as the deterioration of materials by chemical interaction with their environment. Corrosion of metals occurs either by direct chemical attack or by electrochemical attack on the metal by the corrosive environment. The most familiar example of corrosion is rusting of iron exposed to the atmospheric conditions.

$$2Fe(s) + \tfrac{3}{2}O_2(g) + xH_2O(l) \rightarrow \underset{\text{(Chemical composition of rust)}}{Fe_2O_3 \cdot xH_2O(s)}$$

The rusting of iron is a complex chemical reaction that involves both oxygen and moisture (see Fig. 11.12). Iron does not rust in pure water that is oxygen free, and it does not rust in pure oxygen in the absence of moisture. This suggests that the corrosion process is electrochemical in nature. At one place on the surface, iron becomes oxidized in the presence of water and enters solution as Fe^{2+} and this is the anodic location of the metal surface. Reaction taking place at the anode is

$$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$$

The electrons that are released when the iron is oxidized travel through the metal to some other place where the iron is exposed to oxygen. This is the cathodic region of the metal surface where reduction takes place, and oxygen is reduced to give hydroxide ion. The reaction taking place at the cathode is

$$\tfrac{1}{2}O_2(aq) + H_2O(l) + 2e^- \rightarrow 2OH^-(aq)$$

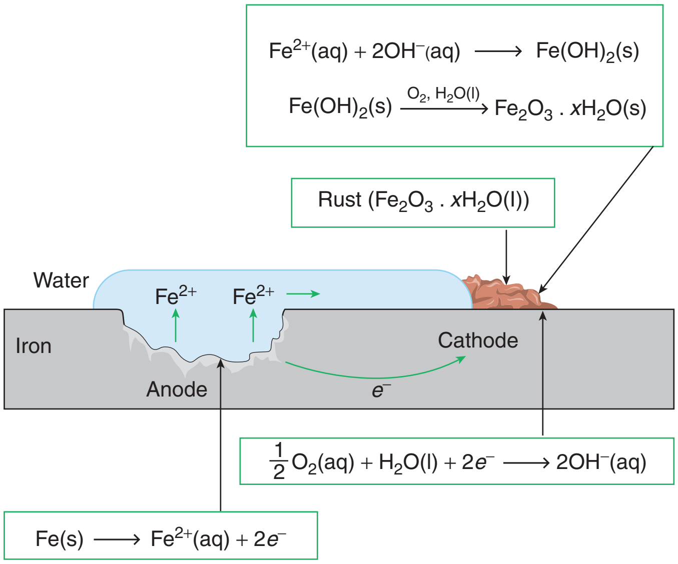

$Fe^{2+}(aq) + 2OH^-(aq) \longrightarrow Fe(OH)_2(s)$
$Fe(OH)_2(s) \xrightarrow{O_2,\ H_2O(l)} Fe_2O_3 . xH_2O(s)$
Rust ($Fe_2O_3 . xH_2O(l)$)
Water
Fe^{2+}
Fe^{2+}
Iron
Cathode
Anode
e^-
$\frac{1}{2}O_2(aq) + H_2O(l) + 2e^- \longrightarrow 2OH^-(aq)$
$Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^-$

Figure 11.12 Corrosion of iron.

The iron (II) ions that are formed at the anodic regions gradually diffuse through the water and eventually contact the hydroxide ions. This causes a precipitate of $Fe(OH)_2$ to form, which is very easily oxidized by O_2 to give $Fe(OH)_3$. This hydroxide readily loses water. In fact, complete dehydration gives the oxide

$$2Fe(OH)_3 \rightarrow Fe_2O_3 + 3H_2O$$

When partial dehydration of the $Fe(OH)_3$ occurs, *rust* is formed. It has a composition that lies between that of the hydroxide and that of the oxide, Fe_2O_3, and is usually referred to as a *hydrated oxide*. Its formula is generally represented as $Fe_2O_3{\cdot}xH_2O$.

The control of corrosion is of great importance to prevent damage to the buildings, bridges, ships and other objects made of iron. It also helps to prevent accidents that may occur due to breaking-up of corroded structures such as bridges and failure of key parts used in machinery. The important methods for control of corrosion are as follows:

1. **Protective coatings (sacrificial protection):** These are used to prevent corrosion at the surfaces of materials. The process involves covering of surface of iron article with a layer of more active metal. The active metal gets oxidized in preference to iron and thus prevents rusting. Protective coatings include metallic coatings, chemical conversion coatings, etc. For example, the tin cans are actually steel cans coated with a thin layer of tin to prevent corrosion of steel; steel objects that must withstand the weather are often coated with a layer of zinc, a process called **galvanization**.
2. **Cathodic protection:** The corrosion of metal takes place at the anodic region whereas at the cathodic region, metal is unaffected. The principle of cathodic protection involves the elimination of anodic sites and conversion of the entire metal into cathodic site. It involves placing the iron in contact with a metal that is *more easily* oxidized. This causes iron to be a cathode and the other metal to be the anode. This anode is known as *sacrifical anode*. If corrosion occurs, iron is protected from oxidation because it is cathodic and the other metal reacts instead. Zinc is most often used to provide cathodic protection to other metals. For example, zinc is attached to the rudder of a boat and when the rudder is submerged, the zinc will gradually corrode but the metal of the rudder will not. Periodically, the anodes are replaced to provide continued protection.

Electroplating

An application of an electrolytic process is the electroplating of one metal onto another. This is done both to protect against corrosion and to improve appearance. For example, a thin layer of silver can be plated onto jewelry or tableware made from a less expensive metal. Figure 11.13 is a schematic diagram of the plating of silver onto a spoon. Oxidation occurs at the silver anode to produce Ag^+ in solution. The Ag^+ ions react with the CN^- ions in solution to form the $[Ag(CN)_2]^-$ complex ion. The $[Ag(CN)_2]^-$ is reduced at the cathode to form a thin layer of silver on the iron spoon. The half-reaction at the cathode is given below.

$$[Ag(CN_2)]^-(aq) + e^- \rightleftharpoons Ag(s) + 2CN^-(aq)$$

The $[Ag(CN)_2]^-$ complex ion is used because it produces a more uniform plating than the direct reduction of a metal cation (Ag^+ ion).

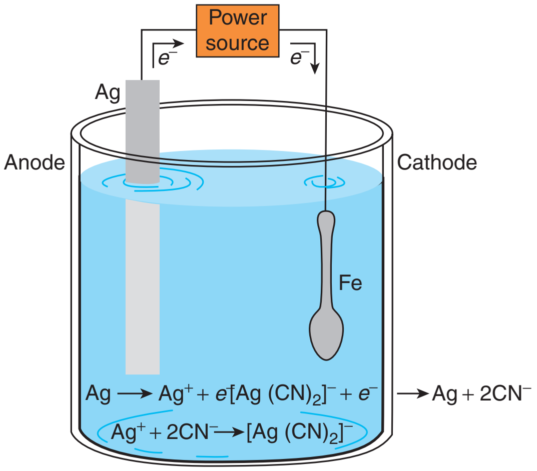

Power source
e^-
e^-
Ag
Anode
Cathode
Fe
$Ag \longrightarrow Ag^+ + e^-$
$[Ag(CN)_2]^- + e^- \longrightarrow Ag + 2CN^-$
$Ag^+ + 2CN^- \longrightarrow [Ag(CN)_2]^-$

Figure 11.13 The plating of silver onto a spoon.

Purification of Metals

A simple electrolytic cell may be constructed by dipping two copper strips in a solution of copper salt. Such a cell is used in purification of impure copper obtained from its ore. The impure copper (containing zinc, iron, silver and gold as impurities) is used as the anode in an electrolytic cell that contains a solution of copper sulphate and sulphuric acid as the electrolyte (see Fig. 11.14). The cathode is a thin sheet of very pure copper. When the cell is operated at the correct voltage, only copper and impurities more easily oxidized than copper (iron and zinc) dissolve at the anode. The less active metals simply fall off the electrode and settle to the bottom of the container. At the cathode, copper ions are reduced, but the zinc ions and iron ions remain in solution because they are more difficult to reduce than copper. Gradually, the impure copper anode dissolves and the pure copper cathode, grows larger.

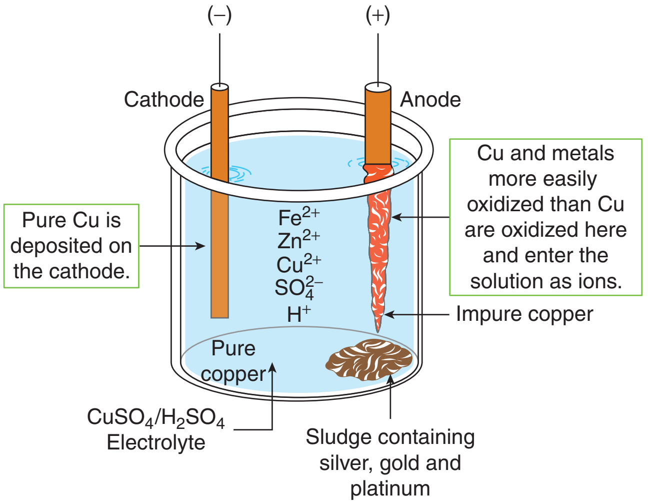

(–)
(+)
Cathode
Anode
Pure Cu is deposited on the cathode.
Fe^{2+}
Zn^{2+}
Cu^{2+}
SO_4^{2-}
H^+
Cu and metals more easily oxidized than Cu are oxidized here and enter the solution as ions.
Impure copper
Pure copper
$CuSO_4/H_2SO_4$ Electrolyte
Sludge containing silver, gold and platinum

Figure 11.14 Purification of copper.

Electrometallurgy

The process of electrolysis is used for extraction of alkali and alkaline earth metals and aluminium from their fused salt solutions. This process involves electrolytic reduction of fused salt solutions, and processes such as Hall–Heroult process, cyanide process, hydrometallurgy adopt this technique. The aqueous solution of these metals salts on cannot be electrolyzed directly because the reduction potential of these metals is low as compared to that of hydrogen ions. Thus reduction of hydrogen ions or water takes place at the cathode.

Preparation of Compounds

The process of electrolysis is used in synthesis of a number of organic compounds. For example, hydrocarbons are prepared by Kolbe's method which involves electrolysis of salts of carboxylic acids. Similarly compounds like aniline, *p*-amino phenol and benzidine are obtained by electrolytic reduction of nitrobenzene in weakly acid, strong acid and alkaline medium, respectively.

Non-metals such as hydrogen, chlorine, fluorine are also obtained by electrolysis. Inorganic compounds such as sodium hydroxide, sodium carbonate, potassium permanganate, etc. are also manufactured by electrolytic processes. $KMnO_4$ is manufactured on a large scale by the alkaline oxidative fusion of MnO_2 (*pyrolusite ore*) followed by electrolytic oxidation in alkaline medium. Some examples of processes using this technique are Down's cell process, Solvay's process, Castner–Kellner cell process.

11.11 | BATTERIES

Electrochemical cells used for conversion of chemical energy into electrical energy are called batteries. A battery is a combination of cells either in series or parallel or both, in order to get the required amount of electrical energy. It is a portable source of electrical energy. In modern times, the words cell and battery are used interchangeably.
The galvanic cells used to form batteries can be classified as:

1. **Primary cells:** In these cells, the chemical energy is converted into electrical energy as long as the chemical components are active. Once the active chemical components are used up, they cannot be regenerated or reused. These cells are then not rechargeable.
2. **Secondary cells:** In these cells, the redox reaction that converts chemical energy into electrical energy can be reversed by passage of current. These cells can be recharged and reused. The electrical energy is stored in them in form of chemical energy and hence these are also known as storage cells. These cells behave as a galvanic cell during discharge, converting chemical energy into electrical and as electrolytic cell during charging, converting electrical energy into chemical energy.

The basic components of a battery are

1. **Anode:** It contains active materials which spontaneously take part in the oxidation reactions.
2. **Cathode:** It contains active materials which spontaneously take part in the reduction reactions.
3. **Electrolyte:** It helps in the migration of the ions leading to the generation of electrical energy.
4. **Separator:** It is a thin polymeric membrane which prevents the mixing of products formed at the electrodes. Usually, polypropylene and polystyrene separators are used.

Primary Cells

Dry Cell

This cell, also known as **Leclanche cell**, consists of a cylindrical zinc container which acts as the anode. A graphite rod surrounded by a paste of manganese dioxide acts as the cathode. These are in contact with a thick paste of ammonium chloride and zinc chloride which acts as the electrolyte (Fig. 11.15). The cell reactions are:

At the anode: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

At the cathode: $MnO_2(s) + H_2O(l) + 2e^- \rightarrow Mn_2O_3(s) + 20H^-(aq)$

Overall cell reaction: $Zn(s) + 2MnO_2(s) + H_2O(l)$
$\rightarrow Zn^{2+}(aq) + Mn_2O_3(s) + OH^-(aq)$

Some secondary reactions take place in the cells which do not contribute to the EMF of the cell as they do not occur at the electrodes. The hydroxyl ions generated at the cathode react with NH_4Cl to liberate ammonia which reacts with Zn^{2+} to form the complex $[Zn(NH_3)]Cl_2$. These processes disrupt the flow of current.

A dry cell develops a potential of 1.5 V and the voltage decreases with usage due to accumulation of products at the electrodes. Even when the cell is not in use, the lifetime of the dry cell is not indefinite because acidic NH_4Cl corrodes the zinc cathode. Dry cells are most commonly used batteries that find use in flash lights, radios, tape recorders, transistors, etc.

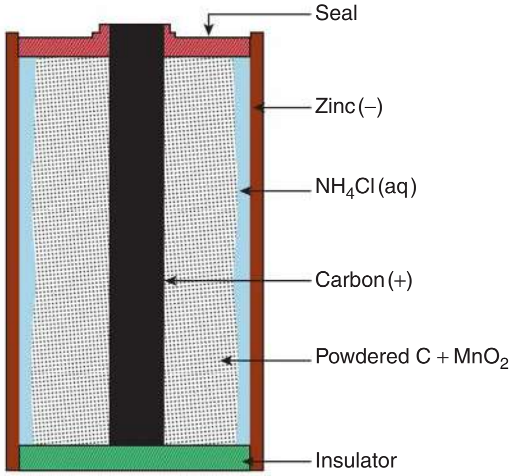


Figure 11.15 Leclanche cell.

Alkaline Dry Cell

This cell is same in construction as the dry cell but modified to replace NH_4Cl as electrolyte by sodium hydroxide or potassium hydroxide, hence the name alkaline dry cell. Replacing NH_4Cl with NaOH/KOH prevents corrosion of zinc cathode since it does not dissolve in basic medium. The cell reactions are:

At the anode: $Zn(s) + 2OH^-(aq) \rightarrow ZnO(s) + H_2O(l) + 2e^-$

At the cathode: $2MnO_2 + 2e^- + H_2O(l) \rightarrow Mn_2O_3(s) + 2OH^-(aq)$

Overall cell reaction: $Zn(s) + 2MnO_2(s) \rightarrow ZnO(s) + Mn_2O_3(s)$

Weston Cadmium Cell

This is a wet chemical cell invented by Edward Weston in 1893, and was adopted as the International Standard for EMF till 1990. This cell, also known as cadmium cell consists of amalgamated cadmium powder that functions as the anode. The cathode comprises pure mercury with a paste of mercurous sulphate with some amount of mercury. A standard solution of cadmium sulphate octa hydrate forms the electrolyte. The cell can be represented as

$$Cd(Hg)|3CdSO_4 \cdot 8H_2O(s)|\text{std. sol. of } CdSO_4(l)\ Hg_2SO_4(s)|Hg$$

For a Weston cadmium cell, $E^\circ = 1.0098$ V at 293 K. The cell reactions are:

At the anode: $Cd(s) \rightarrow Cd^{2+}(aq) + 2e^-$

At the cathode: $\overset{2+}{Hg}\,\overset{2-}{S}O_4(s) + 2e^- \rightarrow 2Hg(l) + SO_4^{2-}(aq)$

Overall cell reaction: $Cd(s) + HgSO_4(s) \rightarrow Cd^{2+}(aq) + 2Hg(l) + SO_4^{2-}(aq)$

Mercury Cell

This cell, also known as **Ruben–Mallory cell** after the inventors, consists of amalgamated zinc powder that functions as the anode. The cathode comprises paste of mercuric oxide with some amount of graphite. A paste of zinc oxide and potassium hydroxide forms the electrolyte (Fig. 11.16).

The cell reactions are:

At the anode: $Zn(s) + 2OH^-(aq) \rightarrow ZnO(s) + H_2O(l) + 2e^-$

At the cathode: $HgO(s) + H_2O(l) + 2e^- \rightarrow Hg(s) + 2OH^-(aq)$

Overall cell reaction: $Zn(s) + HgO(s) \rightarrow ZnO(s) + Hg(s)$

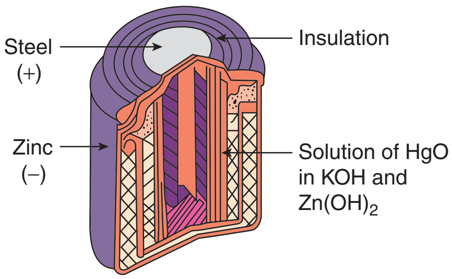


Figure 11.16 Mercury cell.

The zinc cell develops a potential of 1.35 V. It is compact in size because the zinc anode can be compressed into pellet form; the cathode material, mercury oxide, is dense; and the electrolyte KOH is non-variant and thus required in minimal amount. It gives constant potential throughout its lifetime and shows good performance at high temperatures. It is however, expensive due to the high cost of mercury oxide. These cells are used in electronic watches, hearing aids, microphones, cameras, etc.

Secondary (Storage) Cells

Lead Storage Cell (Lead–Acid Battery)

This cell, also known as **acid storage cell**, is the common automobile battery. Its present form is a variant of lead–acid accumulator first designed in 1859. Lead storage cell consists of lead grid filled with spongy lead which acts as the anode and a lead grid packed with lead oxide that acts as the cathode. A set of (generally six) such electrode pairs are dipped in sulphuric acid solution (20%) which acts as the electrolyte and these are separated by inert and porous partitions (Fig. 11.17).

The cell reactions are:

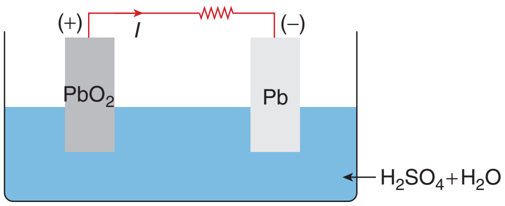


Figure 11.17 Lead–acid battery.

At the anode: $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(aq) + 2e^-$

At the cathode: $PbO_2(s) + 4H^+(aq)\ SO_4^{2-}(aq) + 2e^- \rightarrow PbSO_4(aq) + 2H_2O(l)$

Overall cell reaction: $Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(aq) + 2H_2O(l)$

The cell reaction shows that the electrolyte H_2SO_4 is consumed during the reaction, so as the reaction proceeds, the concentration of H_2SO_4 decreases. Once the concentration of H_2SO_4 has fallen to a certain permissible level, the battery needs to be recharged by reversing the discharge reaction. For this purpose, an external potential higher than the cell potential is applied. The cell then operates like an electrolyte cell and the $PbSO_4$ deposited on the electrodes is reverted to Pb and PbO_2 by the following reactions:

At the anode: $PbSO_4(aq) + 2\,H_2O(l) \rightarrow PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq)$

At the cathode: $PbSO_4(aq) + 2e^- \rightarrow Pb(s) + SO_4^{2-}(aq)$

Overall cell reaction: $2PbSO_4(aq) + 2H_2O(l) \rightarrow Pb + PbO_2(s) + 4H^+(aq) + 2SO_4^{2-}(aq)$

The cell reactions show that the concentration of H_2SO_4 increases during recharging of the cell. The potential developed by each electrode pair is about 2 V and higher potential can be obtained by connecting a number of electrode pairs in series. These batteries find extensive use as automobile batteries, besides being used for electrical supply in trains, hospitals, etc.

Nickel–Cadmium Cell

This cell, also known as **alkaline storage battery**, consists of anode grid which contains spongy cadmium with cadmium hydroxide. The cathode grid contains nickel oxyhydroxide along with small amounts of graphite and other compounds. A concentrated solution of potassium hydroxide acts as an electrolyte (Fig. 11.18)

At the anode: $Cd(s) + 2OH^-(aq) \rightarrow Cd(OH)_2(aq) + 2e^-$

At the cathode: $2NiO(OH)(aq) + 2H_2O(l) + 2e^- \rightarrow 2Ni(OH)_2(aq) + 2\,OH^-(aq)$

Overall cell reaction: $Cd(s) + 2NiO(OH)(aq) + 2\,H_2O(l) \rightarrow 2Ni(OH)_2(aq) + Cd(OH)_2(aq)$

As the reaction proceeds, the products $Ni(OH)_2$ and $Cd(OH)_2$ stick to the surface of the electrode. The cell can be recharged by reversing the reactions. This cell gives potential of about 1.4 V. It can be made into compact button cell type battery and finds use in pocket calculators, electronic flash lights, emergency lights, portable electronics, toys, etc.

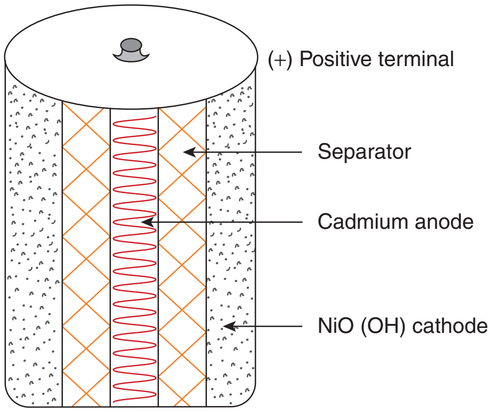


Figure 11.18 Nickel–cadmium cell.

Lithium Batteries

Lithium is a light metal with low electrode potential and good conductivity. It is, therefore, a good material for batteries, and can be expected to have high potential and high energy density. The group of batteries where lithium is used as an anode are known as lithium batteries and they were commercialized in 1990. A large number of lithium batteries are available which have lithium as anode but differ in choice of cathode and electrolyte. These may also be classified as primary or secondary. The most well-known of lithium batteries, lithium–manganese dioxide cell is discussed here.
The construction of $Li–MnO_2$ battery is as follows:

1. Anode is composed of lithium.
2. Cathode is composed of heat treated MnO_2.
3. Electrolyte contains a mixture of LiCl, LiBr, $LiAlO_4$ and $LiClO_4$ dissolved in organic solvents like propylene carbonate and is 2-dimethoxyethane.

The cell reactions are as follows:

At the anode: $Li \rightarrow Li^+ + e^-$

At the cathode: $MnO_2 + Li^+ + e^- \rightarrow Li\overset{III}{Mn}O_2$

Overall cell reaction is: $Li + MnO_2 \rightarrow Li\overset{III}{Mn}O_2$

The battery offers an EMF of 3.0 V. These batteries have the following characteristics:

1. The batteries are light in weight and compact.
2. They are known for low maintenance and have high energy density.

These batteries find application in memory backups, automatic cameras and calculators.

Solved Example 11-47

During the discharge of a lead storage battery, the density of H_2SO_4 falls from 1.294 to 1.139 g mL^{-1}. H_2SO_4 of density 1.294 g mL^{-1} is 39% H_2SO_4 by weight and that of density 1.139 g mL^{-1} is 20% H_2SO_4 by weight. The battery holds 3.5 L of acid and volume remains practically constant during the discharge. Calculate the number of ampere hours for which the battery must have been used. The charging and discharging reactions are:

$$Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(aq) + 2e^- \text{ (charging)}$$

$$PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) \rightarrow PbSO_4(aq) + 2H_2O(l) \text{ (discharging)}$$

Solution

From the given reactions, the overall reaction is:

$$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(aq) + 2H_2O(l)$$

1 mol of Pb gets oxidized to 1 mol of Pb^{2+} (in $PbSO_4$). Therefore, 2 mol of H_2SO_4 are consumed using 2 mol of electrons. Now, the number of moles of H_2SO_4 is equal to the number of faradays consumed.

Before discharge:
Mass of sample in 3.5 L of acid $= 3.5 \times 1.294 \times 10^3 = 4529$ g

$$\text{Moles of } H_2SO_4 = \frac{1766.31}{98} = 18.02 \text{ mol}$$

After discharge:

$$\text{Mass of sample} = 1.139 \times 10^3 \times 3.5 = 3986.5 \text{ g}$$

$$\text{Mass of } H_2SO_4 = \frac{20}{100} \times 3986.5 = 797.3 \text{ g}$$

$$\text{Moles of } H_2SO_4 = \frac{797.3}{98} = 8.135 \text{ mol}$$

Overall process:
Moles of H_2SO_4 consumed $= 18.02 - 8.135 = 9.88$ mol
Hence, the number of faradays used $= 9.88$ F
and so charge $= 9.88 \times 96500 = 953833.57$ C
Now, 1 ampere hour = charge passed by one ampere in one hour $= 60 \times 60 = 3600$ C
Hence, the number of ampere hours $= \dfrac{953833.57}{3600} = 264.95$

Fuel Cells

The conversion into electrical energy involves a number of steps and there is loss of energy at every step. The efficiency of the process is around 40%. There is also a viable way of converting the chemical energy of fuel directly into electrical energy through catalytically activated redox reactions. Such devices are called fuel cells. In other words, fuel cells are galvanic cells in which the electrical energy is directly derived from the redox reactions of the fuel. Even though fuel cells were first demonstrated by Sir William Grove in 1839, they became popular only after NASA used them in their spaceships (1950s).

Ever since the start of the space program, enthusiasm has run high for batteries that are fuel cells. By definition, a fuel cell is an electrochemical cell in which a reaction with oxygen is used to generate electrical energy. Fuel cells, therefore, require the continuous feed of a fuel and oxygen, which produces a low-voltage direct current as long as fuel is provided.

The representation of the fuel cell is

Fuel | Electrode | Electrolyte | Electrode | Oxidant

The chemical reactions involved at the electrodes are:

At the anode: Fuel $\rightarrow$ Oxidation product $+ ne^-$

At the cathode: Oxidant $+ ne^- \rightarrow$ Reduction product

Overall cell reaction: Fuel + Oxidant $\rightarrow$ Oxidation product + Reduction product

The frequently used fuels are hydrogen, methanol, ethanol, hydrazine, formaldehyde, carbon monoxide and alkane. The oxidants could be pure oxygen or air. So far, it has not been practical to react hydrocarbons, such as natural gas, in a fuel cell.

Note: Fuel cells have a working efficiency of about 70–75%. The thermodynamic efficiency (η) of a fuel cell is given by the ratio of electrical work done to the enthalpy change associated with the reaction. Mathematically,

$$\text{Efficiency of cell} = \frac{-nFE}{\Delta H} \tag{11.35}$$

Cell reaction always occurs as a spontaneous reaction.

Hydrogen–Oxygen Fuel Cell

This fuel cell combines hydrogen and oxygen to produce electricity, heat and water. It converts chemical energy to electrical energy and thus can be compared to a battery. The only difference being that as long as hydrogen is supplied, it continues to produce electricity without being discharged.

Design and Working

The whole setup consists of chambers (Fig. 11.19). The first chamber serves as an inlet for hydrogen, while the second one serves as an inlet for oxygen. There are two carbon electrodes: Hydrogen passes over the anode and oxygen passes over the cathode. In the middle, is a proton exchange membrane separating the two electrodes from one another, where these two gases can interact with each other. The electrolyte separating the two electrodes is an ion-conducting material, such as concentrated aqueous sodium hydroxide. The following reactions take place at the two electrodes:

At the anode: $2H_2(g) \rightarrow 4H^+(aq) + 4e^-$
At the cathode: $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$
Overall cell reaction: $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

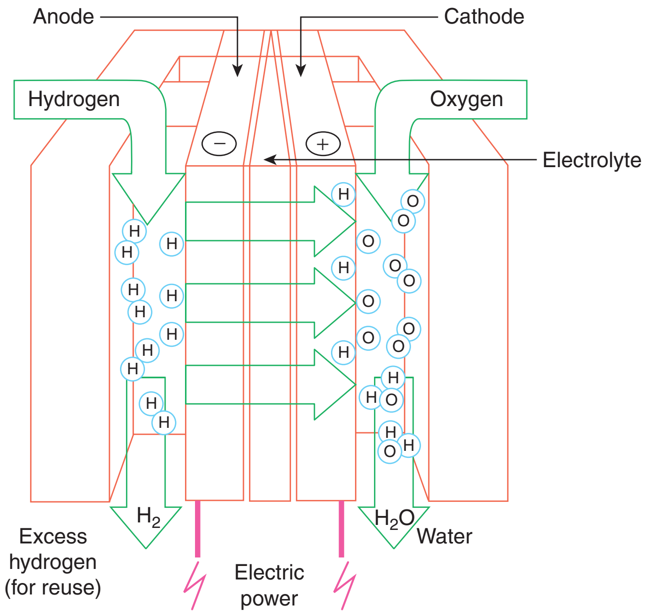


Figure 11.19 A block diagram of hydrogen–oxygen fuel cell.

The water is released in the fourth chamber. The anodic reaction gives protons and electrons. These are separated and hydrogen ions are allowed to pass through the electrolyte to the cathode, while the electrons travel via an external circuit as direct current to power electrical devices. In the cathode, hydrogen ions combine with oxygen to form water along with heat, thus completing the circuit.

Comparison with Conventional Galvanic Cells

Fuel cells differ from the conventional galvanic cells in the following aspects:

1. They consist of two catalytic electrodes.
2. The reagents used are fuel and oxidant.
3. The fuel and oxidant are not stored in the cell. They are stored outside and supplied as and when required.
4. No pollutants are present, and hence fuel cells are environment friendly.
5. No toxic species are formed in a fuel cell.
6. They do not need charging.

Distinct advantages of fuel cells are as follows:

1. They offer high energy conversions (almost 75%).
2. These cells have high energy density.
3. These cells use inexpensive fuels.

Solved Example 11-48

What masses of H_2 and O_2 in grams would have to react each second in a fuel cell at 110°C to provide 1.00 kilowatt (kW) of power if we assume a thermodynamic efficiency of 70%? The reaction is (1 watt = 1 J s^{-1}, [$\Delta H_f^o(H_2O) = -241.8$ kJ; $\Delta S^o(H_2O) = 188.7$ J K^{-1}; $\Delta S^o(H_2) = 130.6$ J K^{-1}; $\Delta S^o(O_2) = 205.0$ J K^{-1})

Solution

The reaction involved is $H_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons H_2O(g)$. The theoretical maximum amount of work is given by the change in free energy:

$$\Delta G = \Delta H - T\Delta S$$

We can find ΔH, ΔS, and T as follows:

$$\Delta H = \Delta H^o_{f(\text{products})} - \Delta H^o_{f(\text{reactants})}$$

$$= (-241.8) - (0 + 0) = -241.8 \text{ kJ}$$

$$\Delta S = \Delta S^o_{\text{products}} - \Delta S^o_{\text{reactants}}$$

$$= (188.7) - [130.6 + (1/2) \times 205.0]$$

$$= -44.4 \text{ J} = -4.4 \times 10^{-2} \text{ kJ}$$

and $$T = 273 + 110 = 383 \text{ K}$$

Substituting these values, we get

$$\Delta G = (-241.8 \text{ kJ}) - 383 \text{ K} \times (-0.0444 \text{ kJ K}^{-1}) = -224.8 \text{ kJ}$$

At 70% efficiency, ΔG becomes $(-224.8) \times (0.70) = -157.4$ kJ (The negative sign simply tells us that work is done by the system.)
Now, 1 kW = 1 kJ s^{-1}. Therefore, we have

$$\text{g } H_2 \text{ s}^{-1} = \left(\frac{1 \text{ kJ}}{1 \text{ s}}\right) \times \left(\frac{1 \text{ mol } H_2}{157.4 \text{ kJ}}\right)\left(\frac{2.016 \text{ g } H_2}{1 \text{ mol } H_2}\right) = 0.01281 \text{ g}$$

$$\text{g } O_2 \text{ s}^{-1} = \left(\frac{1 \text{ kJ}}{1 \text{ s}}\right) \times \left(\frac{0.5 \text{ mol } O_2}{157.4 \text{ kJ}}\right)\left(\frac{32.00 \text{ g } O_2}{1 \text{ mol } O_2}\right) = 0.1065 \text{ g}$$

Solved Example 11-49

In a fuel cell, hydrogen and oxygen react to produce electricity. In the process, hydrogen is oxidized at the anode and oxygen at the cathode. If 67.2 L of H_2 at STP react in 15 min, what is the average current produced? If the entire current is used for electrodeposition of copper from copper (II) solution, how many grams of copper will be deposited?

At the anode: $H_2(g) + 2OH^-(aq) \rightarrow 2H_2O(l) + 2e^-$

At the cathode: $O_2(g) + 2H_2O(l) + 2e^- \rightarrow 4OH^-(aq)$

Solution

Given that 67.2 L of H_2 react at STP which means

$$\frac{67.2}{22.4} = 3 \text{ mol}$$

Quantity of electricity passes for 1 mol = 2 F = 2×96500
And for 3 mol, quantity of electricity passed = 3 × 2 × 96500. As $Q = I \times t$. So,

$$I = \frac{Q}{t} = \frac{3 \times 2 \times 96500}{15 \times 60} = 643.33\ \text{A}$$

Reduction of Cu is given by $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$

2 mol (or 2 × 96500) deposit 63.5 g of Cu

So, 3 mol (or 3 × 2 × 96500) will deposit

$$\frac{63.5 \times 3 \times 2 \times 96500}{2 \times 96500} = 190.5\ \text{g}$$

Solved Example 11-50

For a fuel cell, $\Delta H^\circ = 285.8\ \text{kJ mol}^{-1}$, $\Delta G^\circ = -237.2\ \text{kJ mol}^{-1}$, $E^\circ = 1.23\ \text{V}$. Calculate its thermodynamic efficiency.

Solution

The theoretical efficiency (η) of the fuel cell can be calculated in terms of ΔH and ΔG. Thus,

$$\eta = \frac{\Delta G}{\Delta H} \times 100 = \frac{-237.2\ \text{kJ mol}^{-1}}{-285.8\ \text{kJ mol}^{-1}} \times 100 = 83\%$$

Solved Example 11-51

What volume of H_2 when combined with excess O_2 in the fuel cell at 25°C and 1 atm is needed to produce 47.4 kJ of work under ideal conditions? (Given that $\Delta G^\circ = -237.2\ \text{kJ mol}^{-1}$)

Solution

For ideal conditions, $\Delta G = w_{\text{useful work}}$ = Electrical work. Now,

Number of moles of H_2 required =

$$\frac{\text{Given work}}{\Delta G} = \frac{-47.4}{-237.2} = 0.199\ \text{mol}$$

From the ideal gas equation, $pV = nRT$, we can calculate volume of H_2 as

$$V = \frac{nRT}{p} = \frac{0.199 \times 0.0821 \times 300}{1} = 4.901\ \text{L}$$

11.12 | ELECTRICAL CONDUCTANCE

Substances that allow the passage of current through them are called conductors and the phenomenon is called electrical conductance. Conductors are further divided into two categories, namely, metallic and electrolytic conductors.

Metallic Conductors

In **metallic conductors**, the conductance is only due to the presence of free mobile electrons. Hence, these are also referred to as electronic conductors. This electronic conductance is not accompanied by any chemical change. The passage of current only causes physical changes, and there is no transfer of matter. The factors that affect metallic conductance are as follows:

1. **Temperature:** Metallic conductance is inversely proportional to temperature. As the temperature increases, metallic conduction decreases.
2. **Structure:** The ease of flow of electrons depends on the structure of the metal.
3. **Density:** The denser the metal, lesser will be the metallic conductivity.
4. **Number of valence electrons per atom:** As the number of valence electrons increases, the charge on the metal cation increases; this increases the conductivity.

Electrolytic Conductors

The substances which conduct electricity both in the fused state and in the aqueous solution are called **electrolytic conductors** or **electrolytes**. These substances dissociate in molten state or aqueous solution to furnish ions. The conduction is due to the presence of these mobile ions. For example, molten or aqueous solution of sodium chloride.

Based on the extent of dissociation, electrolytes are classified into two types:

1. **Strong electrolytes:** These electrolytes are almost completely dissociated in their aqueous solutions and have a large value of conductance. For example, HCl, HNO_3, NaOH, KOH, NaCl and KCl.
2. **Weak electrolytes:** These electrolytes which do not undergo complete dissociation even in their dilute aqueous solutions and have low value of conductance. In the solution of a weak electrolyte, there exists an equilibrium between the undissociated molecules and their ions. For example, CH_3COOH, HCOOH and NH_4OH.

   The dissociation of acetic acid is shown as follows:

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

Factors Affecting Electrolytic Conductance

Among the various factors, the following greatly influence the conductance of a solution:

1. **Temperature:** In case of strong electrolytes, increase in temperature increases the speed of the ions. This results in increased conductivity. In case of weak electrolytes, increase in temperature increases the degree of dissociation. There is increase in both the number of ions as well as their speed. Hence, the conductivity increases.
2. **Concentration:** Generally, the conductance of a solution depends on the number of ions present in the solution and the speed of the ions. At higher concentration, the force of attraction between the ions increases, which decreases the speed of the ions. Hence, conductance decreases with increase in concentration.
3. **Nature of electrolyte:** In case the solution is dilute, the ions are farther apart, and their interionic interactions can be neglected; However in a concentrated solution, the interionic interactions are higher, which restricts their free motion, and reduces the conductivity.
4. **Ionic size and their extent of solvation:** In solution state, the solvent–solute interactions are higher, which restricts the free motion of ions, thus decreasing the conductivity. On dilution, these interactions decrease, and ionic mobility, and hence conductance increases.
5. **Viscosity:** In a more viscous solvent, the ionic mobility is low, and thus conductivity of ions is decreased.

> **Note:** The main difference between **metallic** and **electrolytic conductance** is that in metals, the conductance is due to movement of electrons, whereas the conductance in electrolytes is due to ions in solution. There is no transfer of matter or chemical change in metallic conductance, as opposed to electrolytic conductance. Also, metallic conductance decreases with increase in temperature, whereas electrolytic conductance increases with increase in temperature.

11.13 | CONDUCTANCE IN SOLUTIONS OF ELECTROLYTES

In a solution that contains ions (or in a molten ionic compound), *electrical charge is carried through the liquid by the movement of ions, not electrons*. The transport of electrical charge by ions is called **electrolytic conduction**. This conduction is also called solution conductance. The passage of current causes physical as well as chemical changes, and the matter gets transferred in form of ions.

Consider the process of conductance of electrolyte NaCl in an aqueous solution (Fig. 11.20). The aqueous solution consists of Na^+, Cl^-, H^+ and OH^- ions.

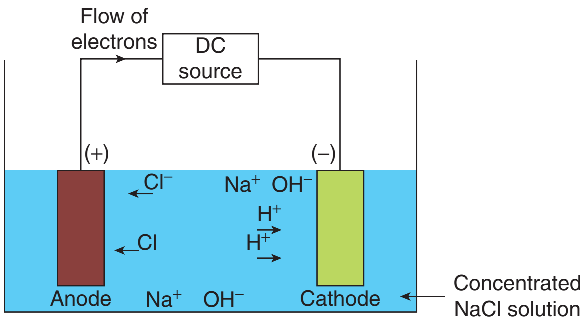


Figure 11.20 Mechanism involved in typical electrolytic conduction.

When electricity is provided by a battery or a DC source, the electrodes acquire electrical charges. They attract ions of opposite charge redox reactions take place at the electrodes. At the anode, the oxidation reaction occurs.

$$Cl^-(aq) \rightarrow \tfrac{1}{2}Cl_2 + e^-$$

The electrons from the anode are pumped through the external circuit. These electrons are delivered to the cathode where reduction occurs:

$$\text{Na}^+(\text{aq}) + e^- \rightarrow \text{Na}$$

The overall effect is that there is a flow of electrons through the external wire resulting from the flow of ions in the solution. The resulting conductance is the electrolytic conductance.

Interionic Attraction Theory of Conductance

Arrhenius postulated in his theory of electrolytic dissociation that in an aqueous solution of an electrolyte, there will be an equilibrium between the ions and the undissociated molecules. This, however, exclusively accounts for the ionic behavior of weak electrolytes only.

The **degree of dissociation (α)** of any electrolyte is defined as:

$$\alpha = \frac{\text{Number of moles of electrolyte dissociated}}{\text{Initial number of moles of electrolyte}} = \frac{x}{n_0} \tag{11.36}$$

In case of a weak electrolyte, addition of water increases the degree of dissociation because water has a high dielectric constant. Increase in the number of ions increases the molar conductivity enormously.

However, molar conductance of a strong electrolyte increases marginally on dilution.

A strong electrolyte contains ions, even in a concentrated solution. The conductance of such a solution is low as each ion is under the influence of other oppositely charged ions. As a result, the ion experiences a *pull* or *drag* in a direction opposite to the direction of flow. The mobility of the ion and hence its conductance will decrease upon dilution, as the distance between the ions increases. The ions experience lesser force of attraction than before. Dilution will not increase the population of ions in the solution but only reduce the force of attraction between them. Hence, the conductance increases marginally.

Electrical Resistance and Conductance

Like any metallic conductor, electrolytic conductor also offers some resistance to the flow of current. The electrical resistance can be measured using a Wheatstone bridge and the unit used is ohm (ohms) which in terms of S.I. base units is equal to (kg m^2)/(s^{3}A^2). Let R be the **resistance** offered by an electrolytic conductor. This resistance is directly proportional to the length (l) of the conductor and inversely proportional to the area of cross-section (A) of the conductor. Therefore,

$$R \propto l \quad \text{and} \quad R \propto \frac{1}{A}$$

So,

$$R \propto \frac{l}{A}$$

or

$$R = \rho \cdot \frac{l}{A} \tag{11.37}$$

where ρ is the proportionality constant. From Eq. (11.37), we have

$$\rho = R \cdot \frac{A}{l}$$

If $R = 1$ ohm, $l = 1$ m and $A = 1$ m^2; then $\rho = R$, where ρ is called the **specific resistance or resistivity**. It is the resistance offered by a conductor of 1 m length and 1 m^2 area of cross-section. In S.I. system, it has unit of ohm m (ohms-meter). According to IUPAC recommendations, the term resistivity is used for specific resistance.

The reciprocal of resistance is known as **conductance** and is represented by G. Mathematically, G is given by

$$G = \frac{1}{R} = \frac{A}{l\rho} \tag{11.38}$$

The S.I. unit of conductance is Siemens, represented by the symbol S and is equal to ohm^{-1}(ohms^{-1}), also called mho.

The reciprocal of specific resistance is called the specific conductance (κ) or conductivity. Therefore,

$$\kappa = \frac{1}{\rho} = \frac{1}{R} \times \frac{l}{A} \tag{11.39}$$

Specific conductance is the conductance of the solution placed between two electrodes having the cross-sectional area of 1 m^2 and placed 1 m apart. In other words, it is defined as the conductance of 1 cm^3 of the solution and has units Siemens per centimeter (S cm^{-1}) in S.I. system. **IUPAC recommends the use of conductivity for specific conductance**. As the specific conductance does not involve the concentration term, it is expressed in the other modes.

Note: The extent of variation of κ with concentration is more pronounced for strong electrolytes as compared to weak electrolytes. In case of strong electrolytes, increase in temperature increases the speed of the ions. This results in increased conductivity. In case of weak electrolytes, increase in temperature increases the degree of dissociation. There is increase in both the number of ions as well as their speed. Hence, the conductivity increases.

Measurement of the Conductance of Ionic Solutions

We have seen that the electrolytic conductivity is given by

$$\kappa = \frac{1}{R} \times \frac{l}{A}$$

Thus, the computation of conductivity would involve measurement of resistance (R) of the electrolyte. We know that any unknown resistance can be measured using a Wheatstone bridge. However, its use for measurement of resistance of an ionic solution poses two problems. The passage of a DC current changes the composition of the solution and it cannot be connected to the bridge as in the case of a metallic wire or a solid conductor. These problems are overcome by using AC current and a specially designed conductivity cell to contain the solution of the electrolyte. This conductivity cell then forms one arm of the circuit which permits the measurement of resistance using the Wheatstone bridge.

The conductivity cell is available in many designs but the essential components are two platinum electrodes of known dimensions, length (l) and area of cross-section (A), coated with platinum black (Fig. 11.21). The ionic solution for which the resistance is to be measured is confined between the two electrodes and its resistance is given by

$$R = \frac{1}{\kappa} \times \frac{l}{A}$$

The ratio of length to the cross-sectional area is called the **cell constant** and it is a characteristic parameter of conductivity of cell used for the experiment.

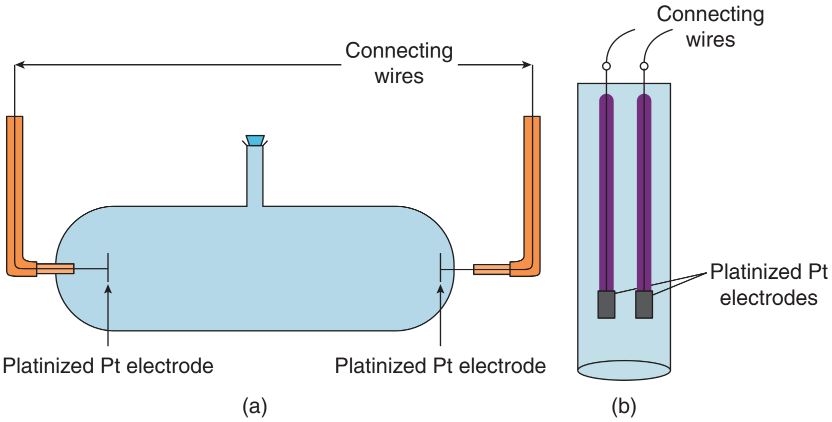


Figure 11.21 Different types of conductivity cells.

$$\text{Cell constant} = \frac{l}{A} \tag{11.40}$$

The cell constant of the conductivity cell is determined by measuring the resistance of a solution of an electrolyte of known conductivity at a given temperature. Generally, a solution of KCl at 298 K is used, for which the conductivity values are reported in literature at different concentrations and temperatures. Once the value of cell constant of a conductivity cell is determined, electrolytic conductivity of any solution can be computed from the measured resistance.

The Wheatstone bridge (Fig. 11.22) set up for measurement of resistance consists of two resistances R_2 and R_3, a variable resistance R_1 and the conductivity cell with unknown resistance R_x. The setup is fed with an AC power and a suitable headphone detector is used. When the bridge is balanced, no current passes through the bridge and therefore, we have

$$I_1R_x = I_2R_1 \quad \text{and} \quad I_1R_3 = I_2R_2$$

Using this relation, we get

$$\frac{I_2}{I_1} = \frac{R_x}{R_1} = \frac{R_3}{R_2}$$

or

$$R_x = \frac{R_1R_3}{R_2}$$

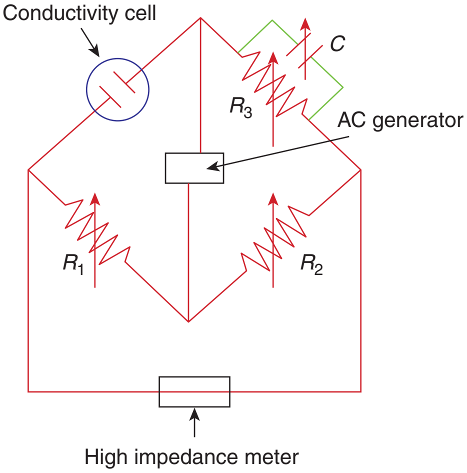


Figure 11.22 Wheatstone bridge.

Thus, if R_1, R_2 and R_3 are known, R_x can be determined and using values of cell constant, the conductivity of the ionic solution can be determined. The conductance of different electrolytes in the same solvent and at a given temperature is different due to difference in nature (charge and size) of ions formed on dissociation of electrolytes. To account for the nature of ions, a more appropriate term (physical quantity) called molar is used to compare conductance of different electrolytes in the same solvent at a given temperature.

Molar and Equivalent Conductance

Molar conductance is defined as the conductance of an electrolytic solution due to all the ions obtained from 1 mol of electrolyte at a given concentration. Mathematically,

$$\Lambda_\mathrm{m} = \frac{\kappa}{1000 \times C} \tag{11.41}$$

where κ is the specific conductance of the solution and C is the molar concentration of the solution. The units of molar conductance in S.I. system are S m^2 mol^{-1}.

Another physical quantity called the **equivalent conductance** is also used. It is the conductance of an electrolytic solution due to all the ions obtained from 1 gram-equivalent (1 g-equiv.) mass of the electrolyte at a given concentration.

Therefore,

$$\Lambda = \kappa V$$

where κ is the conductivity of the solution and V is the volume of the solution containing 1 g-equiv. of the substance. In terms of concentration,

$$\Lambda = \frac{\kappa}{1000 \times C} \tag{11.42}$$

In S.I. system, equivalent conductance has S m^2 g-equiv.$^{-1}$ as the unit.

Effect of Dilution on Molar Conductance

Conductance of a solution depends on the number of ions. It is observed that molar conductance increases upon dilution. This may be due to the increase in the degree of dissociation of the electrolyte or due to decreased ion–ion force of attraction.

With dilution, the influence by other ions on the movement of an ion decreases. At a particular dilution, the ion becomes totally independent of other ions. At this point, it contributes maximum towards the conductance of the solution. The part of the conductance of the solution due to movement of an ion is referred to as **ionic conductance**. Under the conditions, the molar conductance of the solution reaches the maximum value. This value is called **molar conductance at infinite dilution** (Λ_m^0).

The molar conductance at infinite dilution of an electrolyte is the maximum value that an electrolyte can offer. At this point, the conductance is either due to increase in concentration of ions (in a weak electrolyte) or decrease in interionic attraction (in a strong electrolyte). The graphical representation of molar conductance vs. square root of the concentration reinforces this conclusion (Fig. 11.23).

It can be found from the graph that for a strong electrolyte, as the concentration approaches the zero value, the molar conductance approaches a limiting value called molar conductance at infinite dilution. The *y*-intercept made by the curve indicates the molar conductance at infinite dilution.

The curve for a weak electrolyte is a rectangular hyperbola and does not intercept the *y*-axis. Even though the concept of molar conductance at infinite dilution exists for a weak electrolyte, graphically the value cannot be evaluated.

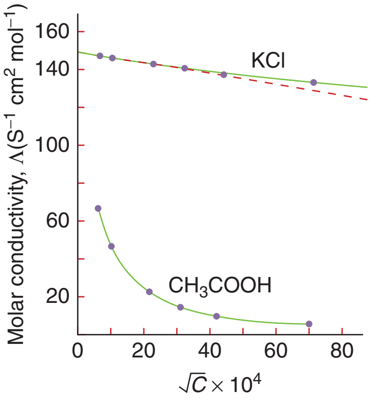


Figure 11.23 Plot of molar conductance vs. (concentration)$^{1/2}$.

Kohlrausch's Law

The variation in molar conductivity with concentration for **strong electrolytes** is given by an empirical relation proposed by **Kohlrausch** based on a number of experimental observations. At low concentrations, the relation is represented by the equation

$$\Lambda_m = \Lambda_m^0 - k\sqrt{C} \tag{11.43}$$

where k is a constant that is specific for a given solvent at a given temperature, but varies with the type of electrolyte, that is, the number of charges on the ions produced by dissociation of the electrolyte. For example, electrolytes like KCl, $MgCl_2$ and $CaSO_4$ are known as 1-1, 1-2, 2-2 types of electrolytes. The value of k for similar type of electrolytes is the same. A plot of Λ_m vs. $\sqrt{C}$ would give a straight line with slope equal to $-k$ and intercept on y-axis equal to Λ_m^0 (Fig. 11.23). Kohlrausch observed certain very interesting relation between the value of Λ_m^0 of different electrolytes having common anion or cation (Table 11.3).

Table 11.3 Molar conductance at infinite dilution of different electrolytes at 298 K, in S m^2 mol^{-1}

Electrolytes	Λ_m^0 (S m^2 mol^{-1})	Difference	Remarks
KCl	14.99×10^{-3}	2.34×10^{-3}	Difference in conductance is due to difference in conductance of K^+ and Na^+ ions
NaCl	12.65×10^{-3}		
KNO_3	14.5×10^{-3}	2.34×10^{-3}	
$NaNO_3$	12.16×10^{-3}		
KCl	14.99×10^{-3}	0.49×10^{-3}	Difference in conductance is due to difference in conductance of Cl^- and NO_3^- ions
KNO_3	14.5×10^{-3}		
NaCl	12.65×10^{-3}	0.49×10^{-3}	
$NaNO_3$	12.16×10^{-3}		
HCl	42.62×10^{-3}	0.49×10^{-3}	
HNO_3	42.13×10^{-3}		

This observation made him formulate the law which states that at infinite dilution when all the interionic effects disappear, each ion makes a definite contribution towards the molar conductivity of the electrolyte irrespective of the nature of the other ion with which it is associated. Mathematically, the law can be stated as

$$\Lambda_m^0 = v_+\lambda_+^0 + v_-\lambda_-^0 \tag{11.44}$$

where Λ_m^0, λ_+^0 and λ_-^0 are limiting molar conductivities of the electrolyte, cations and anions, respectively and ν_+ and ν_- are the number of cations and anions. For example, for $CaCl_2$, the Kohlrausch law of independent migration can be written as

$$\Lambda^0_{m(CaCl_2)} = \lambda^0_{Ca^+} + 2\lambda^0_{Cl^-}$$

> **Note:** The conductivity of a strong electrolyte increases on dilution slightly. This is explained by the **Debye–Huckel–Onsager** equation
>
> $$\Lambda_m = \Lambda_m^0 - (A + B\Lambda_m^0)\sqrt{C}$$
>
> where A and B are the Debye–Huckel constants. If a solution is at infinite dilution, that is, C is almost zero then $\Lambda_m = \Lambda_m^0$.

The variation of molar conductivity of a solution of **weak electrolyte** is not a linear function of the concentration. The molar conductivity increases sharply with decrease in concentration and this is attributed to the increase in degree of dissociation on dilution. Weak electrolytes have a lower degree of dissociation and dissociate to a greater extent in dilute solutions. The number of cations and anions increases thus leading to an increase in molar conductivity. In very dilute solutions, the weak electrolytes also dissociate completely and molar conductivity approaches limiting molar conductivity value (Λ_m^0). However, the values are low and cannot be obtained accurately by extrapolation of curve and Kohlrausch law of independent migration of ions is used to obtain Λ_m^0 for weak electrolytes.

Since molar conductivity depends on the number of free or dissociated ions, we can write degree of dissociation in terms of molar conductivity as

$$\alpha = \frac{x}{n_0} = \frac{\Lambda_m}{\Lambda_m^0}$$

This relation is used to evaluate the degree of dissociation of an electrolyte from the values of molar conductivity at that concentration and limiting value of molar conductivity. Thus, at any concentration (C) the degree of dissociation is

$$\alpha = \frac{\Lambda_m}{\Lambda_m^0} \tag{11.45}$$

where Λ_m is obtained by measurement of resistance in a conductivity cell and Λ_m^0 is evaluated from Kohlrausch law of independent migration of ions. For a weak electrolyte, the dissociation constant at concentration C is given by

$$K = \frac{(C\alpha)(C\alpha)}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$$

Using value of α from Eq. (11.45), we get

$$K = \frac{C\Lambda_m^2}{(\Lambda_m^0)^2\left(1 - \dfrac{\Lambda_m}{\Lambda_m^0}\right)} = \frac{C\Lambda_m^2}{\Lambda_m^0(\Lambda_m^0 - \Lambda_m)} \tag{11.46}$$

Applications of Kohlrausch Law of Independent Ionic Migration

1. **To calculate the Λ_m^0 of weak electrolytes:** The Λ_m^0 values of strong electrolytes can be graphically obtained, while those of weak electrolytes are calculated indirectly by knowing Λ_m^0 values of selected strong electrolytes. The law can be used in evaluating molar conductivity at infinite dilution for weak electrolytes from the individual values of limiting molar conductivities of the ions. For example, if Λ_m^0 of HCl, NaCl and CH_3COONa are known then Λ_m^0 of acetic acid can be calculated as

$$\begin{aligned}\Lambda^0_{(CH_3COOH)} &= \lambda^0_{(CH_3COO^-)} + \lambda^0_{(H^+)}\\ &= \Lambda^0_{(HCl)} + \Lambda^0_{(CH_3COONa)} - \Lambda^0_{(NaCl)}\\ &= \lambda^0_{(H^+)} + \lambda^0_{(Cl^-)} + \lambda^0_{(CH_3COO^-)} + \lambda^0_{(Na^+)} - \left[\lambda^0_{(Na^+)} + \lambda^0_{(Cl^-)}\right]\end{aligned}$$

2. **To calculate the ionic conductance:** The ionic conductance (λ_+^0) can be calculated provided the transport number and molar conductance at infinite dilution are known.

$$t_+ = \frac{(\lambda_+^0)}{\Lambda^0} \tag{11.47}$$

where t_+ is the transport number of the ion.

3. **To calculate the solubility of the sparingly soluble salt:** A saturated solution of a sparingly soluble salt is a very dilute solution. If the specific conductance of the solution is determined, the concentration of the solution can be calculated.

$$\Lambda_m^0 = \frac{\kappa}{1000 \times C} \tag{11.48}$$

The molar conductance at infinite dilution can be obtained from Table 11.3.

For example, given that:

$$K_{\text{AgCl(aq)}} = x \text{ and } K_{\text{H}_2\text{O}} = y$$
$$\lambda^0_{\text{Ag}^+} = W_1 \text{ and } \lambda^0_{\text{Cl}^-} = W_2$$

We have to determine $K_{\text{sp(AgCl)}}$. We know that for any sparingly soluble salt

$$\Lambda = \Lambda^\infty$$

Therefore,

$$K_{\text{AgCl(s)}} \times \frac{100}{S} = \lambda^\infty_{\text{Ag}^+} + \lambda^\infty_{\text{Cl}^-}$$
$$K_{\text{AgCl(s)}} = K_{\text{AgCl(aq)}} - K_{\text{H}_2\text{O}} = x - y$$

Since,

$$S = \sqrt{K_{\text{sp(AgCl)}}}$$

Therefore,

$$(x-y) \times \frac{1000}{\sqrt{K_{\text{sp(AgCl)}}}} = W_1 + W_2$$

4. **Calculation of K_w of water:** Given that $\lambda^\infty_{\text{H}_2\text{O}} = x$ and $K_{\text{H}_2\text{O}} = y$. Then

$$\kappa \times \frac{1000}{C} = \Lambda$$
$$\kappa = \Lambda \times \frac{C}{1000}$$
$$K_{\text{H}^+} = \frac{\lambda_{\text{H}^+}[\text{H}^+]}{1000}$$
$$K_{\text{OH}^-} = \frac{\lambda_{\text{OH}^-}[\text{OH}^-]}{1000}$$
$$K_{\text{H}_2\text{O}} = K_{\text{H}^+} + K_{\text{OH}^-} = \frac{\lambda_{\text{H}^+}[\text{H}^+] + \lambda_{\text{OH}^-}[\text{OH}^-]}{1000}$$

Since H_2O is a weak electrolyte

$$\lambda_{H^+} = \lambda^{\infty}_{H^+} \quad \text{and} \quad \lambda_{OH^-} = \lambda^{\infty}_{OH^-}$$

$$[H^+] = [OH^-] = \sqrt{K_w}$$

Therefore,

$$K_{H_2O} = \frac{\sqrt{K_w}\,[\lambda^{\infty}_{H^+} + \lambda^{\infty}_{OH^-}]}{1000}$$

$$K_w = \left(1000 \times \frac{K_{H_2O}}{\lambda^{\infty}_{H_2O}}\right)^2 = \left(1000 \times \frac{y}{x}\right)^2$$

Note: While using Kohlrausch's law for writing molar conductivities, we use the number of cations and anions, but while using Kohlrausch's law for limiting equivalent conductivities, we do not use the number of cations and anions.

For example, for the reaction

$$BaCl_2 \rightleftharpoons Ba^{2+} + 2Cl^-$$

$$\lambda^{\infty}_{M(BaCl_2)} = \lambda^{\infty}_{M(Ba^{2+})} + 2\lambda^{\infty}_{M(Cl^-)}$$

$$\lambda^{\infty}_{E(BaCl_2)} = \lambda^{\infty}_{E(Ba^{2+})} + \lambda^{\infty}_{E(Cl^-)}$$

Solved Example 11-52

Calculate the specific conductance (κ) of a solution which is placed between two electrodes 1.63×10^{-2} m apart and having cross-sectional area 3.996×10^{-4} m^2. The resistance offered by the solution is 17.69 ohms.

Solution

If the resistance offered by the solution is 17.69 ohms, then

$$\kappa = \frac{1}{R} \times \frac{l}{a} = \frac{1}{17.69} \times \frac{1.63 \times 10^{-2}}{3.996 \times 10^{-4}} = 2.3058 \text{ S m}^{-1}$$

Solved Example 11-53

At 298 K, the specific conductance of 0.1 N NaCl is 1.1 S m^{-1}. Calculate the equivalent conductance at the same temperature.

Solution

Given that $C = 0.1$ N and $\kappa = 1.1$ S m^{-1}. Therefore,

$$\Lambda = \frac{\kappa}{1000 \times C} = \frac{1.1}{1000 \times 0.1} = 1.1 \times 10^{-2}\,\text{S m}^2\text{ g-equiv.}^{-1}$$

Solved Example 11-54

Calculate the molar conductance of infinite dilution of acetic acid at 298 K using the given data: $\Lambda^0_{(HCl)}$, $\Lambda^0_{(CH_3COONa)}$ and $\Lambda^0_{(NaCl)}$ at 298 K as 42.62×10^{-3} S m^2 mol^{-1}, 9.1×10^{-3} S m^2 mol^{-1} and 12.65×10^{-3} S m^2 mol^{-1}, respectively.

Solution

From Kohlrausch's law, we have

$$\begin{aligned}\Lambda^0_m(CH_3COOH) &= \Lambda^0_{(HCl)} + \Lambda^0_{(CH_3COONa)} - \Lambda^0_{(NaCl)}\\ &= 42.62 \times 10^{-3} + 9.1 \times 10^{-3} - 12.65 \times 10^{-3}\\ &= 39.07 \times 10^{-3}\ \text{S m}^2\text{ mol}^{-1}\end{aligned}$$

Solved Example 11-55

Calculate the molar conductivity at infinite dilution of a solution of CH_3COOK from the following data:

$$\Lambda^0_{(HNO_3)} = 421\ \text{S cm}^2\text{mol}^{-1},$$
$$\Lambda^0_{(CH_3COONa)} = 91\ \text{S cm}^2\text{mol}^{-1}$$
and $$\Lambda^0_{(KNO_3)} = 145\ \text{S cm}^2\text{mol}^{-1}, \text{ respectively.}$$

Solution

By Kohlrausch law, we have

$$\Lambda^0_{(CH_3COOK)} = \lambda^0_{(CH_3COO^-)} + \lambda^0_{K^+}$$

Given that

$$\Lambda^0_{(CH_3COOH)} = \lambda^0_{(CH_3COO^-)} + \lambda^0_{(H^+)} = 390\ \text{S cm}^2\ \text{mol}^{-1} \quad (1)$$
$$\Lambda^0_{(KNO_3)} = \lambda^0_{K^+} + \lambda^0_{NO_3^-} = 145\ \text{S cm}^2\ \text{mol}^{-1} \quad (2)$$
$$\Lambda^0_{(HNO_3)} = \lambda^0_{H^+} + \lambda^0_{NO_3^-} = 421\ \text{S cm}^2\ \text{mol}^{-1} \quad (3)$$

Adding Eq. (1) and Eq. (2) and subtracting from Eq. (3), we get

$$\lambda^0_{CH_3COO^-} + \lambda^0_{H^+} + \lambda^0_{K^+} + \lambda^0_{NO_3^-}$$
$$-(\lambda^0_{H^+} + \lambda^0_{NO_3^-}) = 390 + 145 - 421\ \text{S cm}^2\ \text{mol}^{-1}$$
$$\lambda^0_{CH_3COO^-} + \lambda^0_{K^+} = 114\ \text{S cm}^2\ \text{mol}^{-1}$$

Thus molar conductivity at infinite dilution of a solution of CH_3COOK is 114 S cm^2 mol^{-1}.

Solved Example 11-56

The Λ^0_m values for NaCl and KCl are 126.5 S cm^2 mol^{-1} and 149.9 S cm^2 mol^{-1}, respectively. The ionic conductance of Na^+ at infinite dilution is 50.1 S cm^2 mol^{-1}. Calculate the ionic conductance at infinite dilution for K^+ ion.

Solution

Given that

$$\Lambda^0_{m(NaCl)} = 126.5\ \text{S cm}^2\text{mol}^{-1},\ \Lambda^0_{m(KCl)} = 149.9\ \text{S cm}^2\ \text{mol}^{-1}.$$

Thus, we have

$$\Lambda^0_{m(KCl)} - \Lambda^0_{m(NaCl)} = \lambda^0_{(K^+)} - \lambda^0_{m(Na^+)}$$

or $$\lambda^0_{(K^+)} - \lambda^0_{(Na^+)} = 149.9 - 126.5 = 23.4\ \text{S cm}^2\ \text{mol}^{-1}$$

Therefore,

$$\lambda^0_{(K^+)} = 23.4 + \lambda^0_{(Na^+)} = 23.4 + 50.1 = 73.5\ \text{S cm}^2\text{mol}^{-1}.$$

Solved Example 11-57

The molar conductivity of acetic acid solution at infinite dilution is 390.7 S cm^2 mol^{-1}. Calculate the molar conductivity of 0.01 M acetic acid solution, given that the dissociation constant of acetic acid is 1.8×10^{-5}.

Solution

Consider the reaction

$$\begin{array}{rccc} & CH_3COOH \rightleftharpoons & CH_3COO^- + & H^+ \\ \text{Initial moles} & C & 0 & 0 \\ \text{Moles after equilibrium} & C(1-\alpha) & C\alpha & C\alpha \end{array}$$

The equilibrium constant is given by $K = \dfrac{C\alpha^2}{1-\alpha}$

Taking $1 - \alpha = 1$, we get $K = C\alpha^2$. So,

$$\alpha = \left(\frac{K}{C}\right)^{1/2} = \frac{\Lambda_m}{\Lambda^0_m}$$

Substituting the values, we get

$$\frac{\Lambda_m}{390.7} = \left(\frac{1.8 \times 10^{-5}}{0.01}\right)^{1/2} = 4.243 \times 10^{-2}$$

or $$\Lambda_m = 390.7 \times 4.243 \times 10^{-2} = 16.57\ \text{S cm}^2$$

Solved Example 11-58

From the following molar conductivities at infinite dilution, Λ^0_m for $Ba(OH)_2$ = 457 S cm^2 mol^{-1}, Λ^0_m for $BaCl_2$ = 240.6 S cm^2 mol^{-1} and Λ^0_m for NH_4Cl = 2129.8 S cm^2 mol^{-1}. Calculate Λ^0_m for NH_4OH.

Solution

The expressions are

$$\Lambda_{\text{m}}^{0}(\text{Ba(OH)}_2) = \lambda^{0}_{\text{Ba}^{2-}} + 2\lambda^{0}_{\text{OH}^-} \qquad (1)$$

$$\Lambda_{\text{m}}^{0}(\text{BaCl}_2) = \lambda^{0}_{\text{Ba}^{2+}} + 2\lambda^{0}_{\text{Cl}^-} \qquad (2)$$

$$\Lambda_{\text{m}}^{0}(\text{NH}_4\text{Cl}) = \lambda^{0}_{\text{NH}_4^+} + \lambda^{0}_{\text{Cl}^-} \qquad (3)$$

Dividing Eqs. (1) and (2) by 2 and subtracting them, and adding this difference to Eq. (3), we get

$$\Lambda^{0}_{\text{m(NH}_4\text{OH)}} = \lambda^{0}_{\text{NH}_4^+} + \lambda^{0}_{\text{OH}^-}$$

$$= \frac{1}{2}\Lambda^{0}_{\text{m[Ba(OH)}_2]} - \frac{1}{2}\Lambda^{0}_{\text{m(BaCl}_2)} + \Lambda^{0}_{\text{m(NH}_4\text{Cl)}}$$

$$= \frac{1}{2}\times 457 - \frac{1}{2}240.6 + 2129.8 = 2238\ \text{S cm}^2\ \text{mol}^{-1}$$

Solved Example 11-59

At, 291 K, the molar conductivities at infinite dilution of NH_4Cl, NaOH and NaCl are 129.8, 217.4 and 108.9 S cm^2 mol^{-1}, respectively. If the molar conductivity of a centinormal solution of NH_4OH is 9.33 S cm^2 mol^{-1}, what is the percentage dissociation of NH_4OH at this dilution? Also calculate the dissociation constant of NH_4OH.

Solution

Given that $\Lambda^{0}_{\text{NH}_4\text{Cl}} = 129.8\ \text{S cm}^2\ \text{mol}^{-1}$, $\Lambda^{0}_{\text{NaOH}} = 217.4\ \text{S cm}^2\ \text{mol}^{-1}$ and $\Lambda^{0}_{\text{NaCl}} = 108.9\ \text{S cm}^2\ \text{mol}^{-1}$.
By Kohlrausch's law,

$$\Lambda^{0}_{\text{NH}_2\text{OH}} = \lambda^{0}_{\text{NH}_4^+} + \lambda^{0}_{\text{OH}^-} = \Lambda^{0}_{(\text{NH}_4\text{Cl})} + \Lambda^{0}_{(\text{NaOH})} - \Lambda^{0}_{(\text{NaCl})}$$

$$= 129.8 + 217.4 - 108.9 = 238.3\ \text{S cm}^2\ \text{mol}^{-1}$$

Given that $\Lambda_c = 9.33$ S cm^2 mol^{-1}. Therefore, degree of dissociation is

$$\alpha = \frac{\Lambda_c}{\Lambda^0} = \frac{9.33}{238.3} = 0.0392$$

or the percentage dissociation = 0.0392 × 100 = 3.92%.

Now, the reaction can be represented as

$$\begin{array}{lccc} & \text{NH}_4\text{OH} \rightleftharpoons & \text{NH}_4^+ & +\,\text{OH}^- \\ \text{Initial concentration} & C & 0 & 0 \\ \text{Equilibrium concentration} & C - C\alpha & C\alpha & C\alpha \end{array}$$

The equilibrium constant is

$$K = \frac{C\alpha \times C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$$

Substituting $C = 0.01$ N = 0.01 M and $\alpha = 0.0392$, we get

$$K = \frac{(0.01)(0.0392)^2}{1-0.0392} = \frac{10^{-2}(3.92\times 10^{-2})^2}{0.09608} = 1.599\times 10^{-5}$$

Solved Example 11-60

Calculate the molar conductivity and equivalent conductivity at infinite dilution of potash alum. Given that $\lambda^{0}_{\text{m(K}^+)} = 73.5\ \text{S cm}^2\ \text{mol}^{-1}$, $\lambda^{0}_{\text{m(Al}^{3+})} = 189\ \text{S cm}^2\ \text{mol}^{-1}$ and $\lambda^{0}_{\text{m(SO}_4^{2-})} = 160\ \text{S cm}^2\ \text{mol}^{-1}$

Solution

We find that at infinite dilution, 1 mol of potash alum, $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ will produce 2 mol each of K^+ and Al^{3+} and 4 mol of SO_4^{2-}. Hence, we have

$$\Lambda^{0}_{\text{m[K}_2\text{SO}_4\cdot\text{Al}_2(\text{SO}_4)_3\cdot 24\text{H}_2\text{O]}} = 2\lambda^{0}_{\text{m(K}^-)} + 2\lambda^{0}_{\text{m(Al}^{3+})} + 4\lambda^{0}_{\text{m(SO}_4^{2-})}$$

$$= 2\times 73.5 + 2\times 189 + 4\times 160$$

$$= 147 + 378 + 640 = 1165\ \text{S cm}^2\ \text{mol}^{-1}$$

As the total charge carried by 1 mol of potash alum is 8, then 1 equiv. of the salt will be equal to (1/8) of 1 mol. Thus, we have

$$\Lambda^{0}_{\text{eq(potash alum)}} = \frac{\Lambda^{0}_{\text{eq(potash alum)}}}{8} = \frac{1165}{8} = 145.6\ \text{S cm}^2\ \text{equiv.}^{-1}$$

Solved Example 11-61

We have taken a saturated solution of AgBr. K_{sp} of AgBr is 12×10^{-14}. If 10^{-7} mol of $AgNO_3$ are added to 1 L of this solution, find conductivity (specific conductance) of this solution in terms of 10^{-7} S m^{-1} units. Given, $\lambda^{0}_{(\text{Ag}^+)} = 6\times 10^{-3}\ \text{S m}^3\ \text{mol}^{-1}$, $\lambda^{0}_{(\text{Br}^-)} = 8\times 10^{-3}\ \text{S m}^3\ \text{mol}^{-1}$, $\lambda^{0}_{(\text{NO}_3^-)} = 7\times 10^{-3}\ \text{S m}^3\ \text{mol}^{-1}$.

(IIT-JEE 2006)

Solution

Suppose solubility of AgBr in presence of 10^{-7} M $AgNO_3$ solution is S. Then the reactions involved are

$$\mathrm{AgBr} \rightarrow \underset{S}{\mathrm{Ag}^+} + \underset{S}{\mathrm{Br}^+}$$

$$\mathrm{AgNO_3} \rightarrow \underset{10^{-7}\ \mathrm{M}}{\mathrm{Ag}^+} + \underset{10^{-7}\ \mathrm{M}}{\mathrm{NO_3^-}}$$

The concentration terms $[Ag^+] = [S + 10^{-3}]$ and $[Br] = S$. Now, $K_{sp} = [Ag^+][Br^-]$, substituting values, we get

$$12\times 10^{-14} = (S+10^{-7})S \Rightarrow S^2 + 10^{-7}S + 12\times 10^{-14} = 0$$

which is quadratic in S, solving and ignoring negative root, we get

$$S = \frac{-10^{-7} + \sqrt{10^{-14} + 4\times 12\times 10^{-14}}}{2}$$

$$= \frac{-10^{-7} + 7\times 10^{-7}}{2} = 3\times 10^{-7}\ \mathrm{M}$$

In solution, we have $[Ag^+] = S + 10^{-7} = 3 \times 10^{-7} + 10^{-7} = 4 \times 10^{-7}$ M; $[Br^-] = S = 3 \times 10^{-7}$ M; $[NO_3^-] = 10^{-7}$ M. Now, specific conductance is

$$\kappa = \kappa_{\mathrm{Ag^+}} + \kappa_{\mathrm{Br^-}} + \kappa_{\mathrm{NO_3^-}} = \lambda^0_{(\mathrm{Ag^+})} \times C_{(\mathrm{Ag^+})}$$

$$+ \lambda^0_{(\mathrm{Br^-})} \times C_{(\mathrm{Br^-})} + \lambda^0_{(\mathrm{NO_3^-})} \times C_{(\mathrm{NO_3^-})}$$

$$= 6\times 10^{-3}\times 4\times 10^{-7} + 8\times 10^{-3}\times 3\times 10^{-7} + 7\times 10^{-3}\times 10^{-7}$$

$$= 55\times 10^{-10}\ \mathrm{S\,m^{-1}}$$

11.14 | CONDUCTOMETRIC TITRATIONS

These titrations are based on the fact that during the titration, one of the ions is replaced by the other. Now, these two ions differ in their ionic conductivities, which results in varying conductivity during the course of titration. So, conductometric titrations can be performed in solutions where the ions have difference in conductivities and mobilities. We can have further cases involving differences in acids and bases, etc.

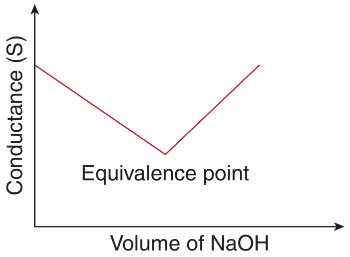


Figure 11.24 Conductometric titration curve of a strong acid (HCl) versus strong base (NaOH).

Strong Acid vs. Strong Base

Consider titration of HCl (strong acid) with NaOH (strong base). Initially with pure HCl, the conductance is very high due to the highly conducting H^+ ions. Now, once we start adding NaOH, H^+ (faster moving) are replaced with Na^+ (slow moving) thereby decreasing the overall conductance till the equivalence point, where we have only NaCl in our solution. Now, if we further add NaOH, then the solution starts having an excess of OH^- ions, which increases the conductivity. Hence, if we plot a graph of conductance versus volume of NaOH added (Fig. 11.24).

Weak Base vs. Strong Acid

When a weak base like NH_4OH is titrated against HCl by taking HCl in the conductance cell. The curve obtained will be of the type shown in Fig. 11.25.

In this titration, a replacement of highly conducting H_3O^+ ions by feebly ionized NH_4^+ occurs as the following reaction proceeds:

$$\mathrm{H_3O^+ + Cl^- + NH_4^+ + OH^- \rightarrow NH_4^+ + Cl^- + 2H_2O}$$

As a result, a fall in conductance is observed up to the end point. After the equivalence point, the conductance remains practically constant because NH_4OH has very low conductance compared to HCl or NH_4Cl. A slight curvature is observed near the end point. This is due to the following reaction

$$\mathrm{NH_4^+ + 2H_2O \rightleftharpoons NH_4OH + H_3O^+}$$

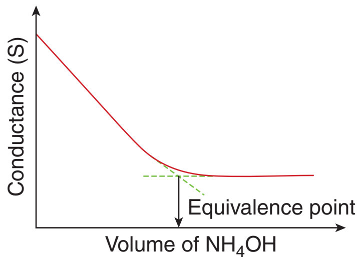


Figure 11.25 Conductometric titration curve of CH_3COOH (weak acid) versus strong base (NaOH).

which shows the generation of very fast moving H_3O^+ ions. It is due to the H_3O^+ ion produced by hydrolysis in the system that the fall in conductance of the solution is arrested and an upward curve in the plot is observed.

Weak Acid vs. Strong Base

The titration curve of a weak acid like CH_3COOH by a strong base NaOH shows a curved portion which is due to the following hydrolysis reaction:

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

Due to the common ion effect of CH_3COONa during the titration, the dissociation of acetic acid is suppressed. Consequently, the conductivity increases as the conducting power of sodium acetate is more than that of the feebly ionized acetic acid. The curvature is not so marked in this case (Fig. 11.26).

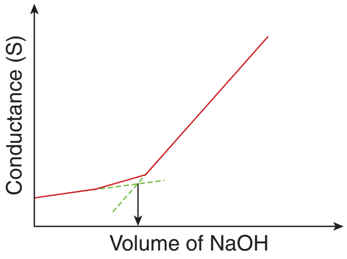


Figure 11.26 Conductometric titration curve of CH_3COOH (weak acid) vs. strong base (NaOH).

Mixture of Acids vs. Strong Base

When a mixture containing both the strong acid (HCl) and a weak acid (CH_3COOH) is titrated with a strong base (NaOH), the conductance of the solution gradually decreases due to the removal of H^+ ions of highly ionized HCl to form unionized water. Subsequently, the feebly ionized weak acid is neutralized. The conductance increases marginally due to the salts produced. After the equivalence point, the increase in conductance is appreciable due to the added OH^- ions (Fig. 11.27). The variation in conductance is an indicator of the trend in the neutralization reaction.

$$Na^+ + OH^- + H^+ + Cl^- \rightarrow Na^+ + Cl^- + H_2O$$

$$CH_3COOH + Na^+ + OH^- \rightarrow CH_3COO^- + Na^+ + H_2O$$

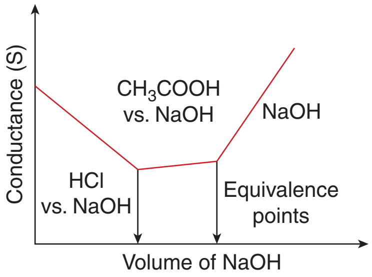


Figure 11.27 Conductometric titration curve of mixture of acids (HCl + CH_3COOH) vs. strong base (NaOH).

AgNO$_3$ vs. NaCl

When NaCl is added to a solution of $AgNO_3$, initially the conductance is high as $AgNO_3$ is a strong electrolyte. But as soon as AgCl is formed, there is a marked drop in the conductance and it remains constant till all $AgNO_3$ is used up as AgCl does not dissociate. After $AgNO_3$ is used completely, there is an increase in conductance as NaCl is free and it is a strong electrolyte (Fig. 11.28).

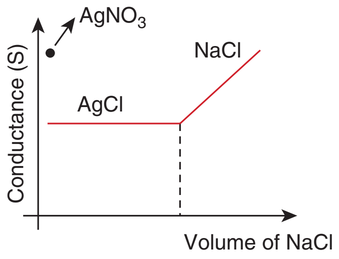


Figure 11.28 Conductometric titration curve of a mixture of $AgNO_3$ and NaCl.

SOLVED OBJECTIVE QUESTIONS FROM PREVIOUS YEAR PAPERS

1. Which of the following statements is correct for an electrolytic cell? **(IIT-JEE 2003)**

(A) Electrons flow from cathode to anode through the external battery.

(B) Electrons flow from cathode to anode within the electrolytic solution.

(C) Migration of ions along with oxidation reaction at cathode and reduction reaction at anode.

(D) Migration of ions along with reduction reaction at cathode and oxidation reaction at anode.

Solution

(D) In an electrolytic cell, electrons do not flow themselves. It is the migration of ions towards oppositely charged electrons that indirectly constitute the flow of electrons from cathode to anode through internal supply.

2. $Zn|Zn^{2+}(a = 0.1\,M)||Fe^{2+}(a = 0.01\,M)|Fe$. The emf of the above cell is 0.2905 V. Equilibrium constant for the cell reaction is **(IIT-JEE 2004)**

(A) $10^{0.32/0.0591}$ (B) $10^{0.32/0.0295}$

(C) $10^{0.26/0.0295}$ (D) $e^{0.32/0.295}$

Solution

(B) Consider the reaction $Zn + Fe^{2+} \rightarrow Zn^{2+} + Fe$

$$E = E^{o}_{cell} - \frac{0.0591}{n}\log K_C$$

$$0.2905 = E^{o}_{cell} - \left(\frac{0.0591}{2}\right)\log\left(\frac{0.1}{0.01}\right)$$

Solving, we get $E^{o}_{cell} = 0.2905 + 0.02905 = 0.32$. Now,

$$E^{o}_{cell} = \left(\frac{0.0591}{n}\right)\log K_C \Rightarrow 0.32 = \left(\frac{0.0591}{2}\right)\log K_C$$

Solving, we get $K_C = 10^{0.32/0.0295}$.

3. From the following data

$$2H^{+}(aq) + \tfrac{1}{2}O_2(g) + 2e^{-} \rightarrow H_2O(l) \quad E^{o}_{cell} = 1.23\,V$$

$$Fe^{2+}(aq) + 2e^{-} \rightarrow Fe(s) \quad E^{o}_{cell} = -0.44\ V$$

show that ΔG^{o} for

$$2Fe(s) + 4H^{+}(aq) + O_2(g) \rightarrow 2Fe^{2+}(aq) + 2H_2O(l) \text{ is}$$

(A) -322.3 kJ mol^{-1} (B) -483.5 kJ mol^{-1}

(C) -644.6 kJ mol^{-1} (D) 644.6 kJ mol^{-1}

(IIT-JEE 2005)

Solution

(C) The reactions involved are

$$2H^{+}(aq) + \tfrac{1}{2}O_2(g) + 2e^{-} \rightarrow H_2O(l) \quad E^{o}_{cell} = 1.23\,V \qquad (1)$$

$$Fe^{2+}(aq) + 2e^{-} \rightarrow Fe(s) \quad E^{o}_{cell} = -0.44\ V \qquad (2)$$

Multiplying Eqs. (1) and (2) by 2, we get

$$4H^{+}(aq) + O_2(g) + 4e^{-} \rightarrow 2H_2O(l) \quad E^{o}_{cell} = 2.46\,V \qquad (3)$$

$$2Fe^{2+}(aq) + 4e^{-} \rightarrow 2Fe(s) \quad E^{o}_{cell} = -0.88\ V \qquad (4)$$

Reverse Eq. (4), we get

$$2Fe(s) \rightarrow 2Fe^{2+}(aq) + 4e^{-} \quad E^{o}_{cell} = +0.88\ V \qquad (5)$$

Adding Eqs. (3) and (5), we get

$$2Fe + 4H^{+} + O_2 \rightarrow 2Fe^{2+} + 2H_2O$$

$$E^{o}_{cell} = 2.46 + 0.88 = 3.34\ V$$

Therefore,

$$\Delta G^{o} = -nFE^{o}_{cell} = -2 \times 96500 \times 3.34 = -644.6\ \text{kJ}\,mol^{-1}$$

4. Read the paragraph below and answer the questions that follow.

Tollens' reagent is used for the detection of aldehyde when a solution of $AgNO_3$ is added to glucose with NH_4OH then gluconic acid is formed

$$Ag^{+}(aq) + e^{-} \rightarrow Ag(s);\ E^{o}_{Ag^{+}/Ag} = 0.8\ V$$

$$C_6H_{12}O_6(s) + H_2O(l) \rightarrow \underset{\text{Gluconic acid}}{C_6H_{12}O_7}(aq) + 2H^{+}(aq) + 2e^{-};$$

$$E^{o}_{red} = -0.05\ V$$

$$[Ag(NH_3)_2]^{+}(aq) + e^{-} \rightarrow Ag(s) + 2NH_3(aq) \quad E^{o}_{red} = 0.337\ V$$

$$\left[\text{Use } 2.303 \times \frac{RT}{F} = 0.0592 \text{ and } \frac{F}{RT} = 38.92 \text{ at } 398\ K\right]$$

(IIT-JEE 2006)

4a. $2Ag^{+}(aq) + C_6H_{12}O_6(s) + H_2O(l) \rightarrow 2Ag(s) + C_6H_{12}O_7(aq) + 2H^{+}(aq)$. Find ln K of this reaction.

(A) 66.13 (B) 58.38

(C) 28.30 (D) 46.29

Solution

(B) $E^{o}_{cell} = \frac{RT}{nF}\ln K$. Substituting values, we get

$$0.8 - 0.05 = \frac{1}{2} \times \frac{0.0592}{2.303}\ln K$$

or

$$\ln K = 0.75 \times 2 \times \frac{2.303}{0.0592} = 58.35$$

4b. When ammonia is added to the solution, pH is raised to 11. Which half-cell reaction is affected by pH and by how much?

(A) E_{ox} will increase by a factor of 0.65 from E^{o}_{ox}

(B) E_{ox} will decrease by a factor of 0.65 from E^{o}_{ox}

(C) E_{red} will increase by a factor of 0.65 from E^{o}_{ox}

(D) E_{red} will decrease by a factor of 0.65 from E^{o}_{ox}

Solution

(C) On increasing the concentration of NH_3, the concentration of H^{+} ions decreases. Therefore, E_{red} increases.

4c. Ammonia is always is added in this reaction. Which of the following must be incorrect?

(A) NH_3 will combines with Ag^{+} to form a complex.

(B) $[Ag(NH_3)_2]^{+}$ is a stronger oxidizing reagent than Ag^{+}.

(C) In absence of NH_3, silver salt of gluconic acid is formed.

(D) NH_3 has affected the standard reduction potential of glucose/gluconic acid electrode.

Solution

(D) It is clear from the reaction that NH_3 combines with Ag to give $[Ag(NH_3)_2]^{+}$. Also, the value of E^{o}_{red} of Ag^{+} is greater than $[Ag(NH_3)_2]^{+}$, which means it is a stronger oxidizing agent than Ag^{+}, and in absence of ammonia, gluconic acid is formed.

5. Read the passage below and answer the questions that follow:

Redox reactions play a pivotal role in chemistry and biology. The values of standard redox potential (E^{o}) of two half-cell reactions decide which way the reaction is expected to proceed. A simple example is a Daniell cell in which zinc goes into solution and copper gets deposited. Given below are a set of half-cell reactions (acidic medium) along with their E^{o}(V) with respect to normal hydrogen electrode values. Using this data obtain the correct explanations to Questions 5a to 5c.

$I_2 + 2e^- \rightarrow 2I^-;$ $E^\circ = 0.54\ V$

$Cl_2 + 2e^- \rightarrow 2Cl^-;$ $E^\circ = 1.36\ V$

$Mn^{3+} + e^- \rightarrow Mn^{2+};$ $E^\circ = 1.50\ V$

$Fe^{3+} + e^- \rightarrow Fe^{2+};$ $E^\circ = 0.77\ V$

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O;$ $E^\circ = 1.23\ V$

(IIT-JEE 2007)

5a. Among the following, identify the correct statement.

(A) Chloride ion is oxidized by O_2
(B) Fe^{2+} is oxidized by iodine
(C) Iodide ion is oxidized by chlorine
(D) Mn^{2+} is oxidized by chlorine

Solution

(C) E° values indicate the reduction potential of the ion/atom. A negative or smaller value of E° means that is acting as a reducing agent or it is getting oxidized as compared to the electrode having higher value of E°. Here, the reduction potential of iodide ion is less than chlorine, so iodide is getting oxidized by chlorine. It could have been oxidized by Mn or O_2 because they too have higher value of reduction potential than iodide.

5b. While Fe^{3+} is stable, Mn^{3+} is not stable in acid solution because

(A) O_2 oxidizes Mn^{2+} to Mn^{3+}
(B) O_2 oxidizes both Mn^{2+} to Mn^{3+} and Fe^{2+} to Fe^{3+}
(C) Fe^{3+} oxidizes H_2O to O_2
(D) Mn^{3+} oxidizes H_2O to O_2

Solution

(D) Reaction of Mn^{3+} with H_2O is spontaneous.

At the anode: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O;\quad E^\circ = 1.23\ V$

At the cathode: $Mn^{3+} + e^- \rightarrow Mn^{2+};\quad E^\circ = 1.50\ V$

$$E_{cell} = E_{cathode} - E_{anode} = 1.50 - 1.23 = 0.27\ V$$

Since E_{cell} is positive, the reaction is spontaneous because Gibbs energy is negative $= -nFE_{cell}$.

5c. Sodium fusion extract, obtained from aniline, on treatment with iron(II) sulphate and H_2SO_4 in presence of air gives a Prussian blue precipitate. The blue color is due to the formation of

(A) $Fe_4[Fe(CN)_6]_3$
(B) $Fe_3[Fe(CN)_6]_2$
(C) $Fe_4[Fe(CN)_6]_2$
(D) $Fe_3[Fe(CN)_6]_3$

Solution

(A) $\underset{}{Fe(OH)_2} + 6NaCN \rightarrow \underset{\text{Sodium ferrocyanide}}{Na_4Fe(CN)_6} + 2NaOH$

$$3Na_4Fe(CN)_6 + 2Fe_2(SO_4)_3 \rightarrow \underset{\text{Prussian blue ppt.}}{Fe_4[Fe(CN)_6]_3} + 6Na_2SO_4$$

6. Read the passage below and answer the questions that follow: Chemical reactions involve interaction of atoms and molecules. A large number of atoms/molecules (approximately 6.023×10^{23}) are present in a few grams of any chemical compound varying with their atomic/molecular masses. To handle such large numbers conveniently, the mole concept was introduced. This concept has implications in diverse areas such as analytical chemistry, biochemistry, electrochemistry and radiochemistry. The following example illustrates a typical case, involving chemical/electrochemical reaction, which requires a clear understanding of the mole concept.

A 4.0 M aqueous solution of NaCl is prepared and 500 mL of this solution is electrolyzed. This leads to the evolution of chlorine gas at one of the electrodes (atomic mass: Na = 23u, Hg = 200u; 1 Faraday = 96500 coulombs)

(IIT-JEE 2007)

6a. The total number of moles of chlorine gas evolved is

(A) 0.5
(B) 1.0
(C) 2.0
(D) 3.0

Solution

(B) The reaction is $NaCl \rightarrow Na^+ + Cl^-$. The reaction at anode is $2Cl^- \rightarrow Cl_2$. The number of moles of $Cl^- = 2$ in 500 mL. Therefore, 1 mol of Cl_2 is evolved.

6b. If the cathode is a Hg electrode, the maximum mass of amalgam formed from this solution is

(A) 200 g
(B) 225 g
(C) 400 g
(D) 446 g

Solution

(D) Na–Hg (amalgam) formed = 2 mol at cathode

$$= (200 + 23) \times 2 = 446\ g.$$

6c. The total charge required for complete electrolysis is

(A) 24125 C
(B) 48250 C
(C) 96500 C
(D) 193000 C

Solution

(D) 2 mol of electrons are required or 2 F of charge is required for complete electrolysis. Now, I F = 96500 C. So, 2 F = 96500 × 2 = 193000 C.

7. Electrolysis of dilute aqueous NaCl solution was carried out by passing 10 milliampere current. The time required to liberate 0.01 mol of H_2 gas at the cathode is (1 Faraday constant = 96500 C mol^{-1}) **(IIT-JEE 2008)**

(A) 9.65×10^4 s
(B) 19.3×10^4 s
(C) 28.95×10^4 s
(D) 38.6×10^4 s

Solution

(B) We know that

$$Q = I \times t = 10 \times 10^{-3} \times t \quad (1)$$

In the reaction $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ to liberate 0.01 mol of H_2, 0.02 F charge is required. The charge $Q = 0.02 \times 96500$ C. Substituting in Eq. (1), we get

$$0.02 \times 96500\ C = \ 10^{-2} \times \ t \Rightarrow t = 19.3 \times 10^4\ \text{s}$$

8. For the reduction of NO_3^- ion in an aqueous solution, E^o is $+0.96$ V. Values of E^o for some metal ions are given below:

$V^{2+}(aq) + 2e^- \rightarrow V;$	$E^o = -1.19$ V
$Fe^{3+}(aq) + 3e^- \rightarrow Fe;$	$E^o = -0.04$ V
$Au^{3+}(aq) + 3e^- \rightarrow Au;$	$E^o = +1.40$ V
$Hg^{2+}(aq) + 2e^- \rightarrow Hg;$	$E^o = +0.86$ V

The pair(s) of metals that is (are) oxidized by NO_3^- in aqueous solution is (are)

(A) V and Hg (B) Hg and Fe
(C) Fe and Au (D) Fe and V

(IIT-JEE 2009)

Solution

(A), (B), (D) $E^o_{NO_3^-} = 0.96$ V and V, Fe, Hg have low value of standard reduction potential with respect to NO_3^-. So, V, Fe, Hg can be oxidized by NO_3^- in aqueous solution.

9. Read the following paragraph and answer the questions that follow:

The concentration of potassium ions inside a biological cell is at least twenty times higher than the outside. The resulting potential difference across the cell is important in several processes such as transmission of nerve impulses and maintaining the ion balance. A simple model for such a concentration cell involving a metal M is: $M(s)\,|\,M^+(aq,\ 0.05\ M)\,\|\,M^+(aq, 1\ M)\,|\,M(s)$. For this electrolytic cell, the magnitude of the cell potential $|E_{cell}| = 70$ mV.

(IIT-JEE 2010)

9a. For the above cell

(A) $E_{cell} < 0; \Delta G > 0$ (B) $E_{cell} > 0; \Delta G < 0$
(C) $E_{cell} < 0; \Delta G^o > 0$ (D) $E_{cell} > 0; \Delta G^o > 0$

Solution

(B) For the given concentration cell

$$E_{cell} = \frac{2.303\ RT}{nF}\log\frac{C_2}{C_1} = \frac{2.303\ RT}{nF}\log\frac{1}{0.05} = +\text{ve}$$

or $E_{cell} > 0$. For the cell reaction to be spontaneous, $\Delta G < 0$.

9b. If the 0.5 M solution of M^+ is replaced by 0.0025 M solution of M^+, then the magnitude of the cell potential would be

(A) 35 mV (B) 70 mV
(C) 140 mV (D) 700 mV

Solution

(C) For the first cell

$$\frac{2.303RT}{F}(1.301) = 0.07 \Rightarrow \frac{2.303RT}{F} = 0.0538$$

For the new cell

$$E_{cell} = \frac{2.303\ RT}{F}\log\frac{1}{0.0025} = 0.0538\log 400$$
$$= 0.0538 \times 2.6021 = 0.140\ \text{V} = 140\ \text{mV}$$

10. Consider the following cell reaction:

$$2Fe(s) + O_2(g) + 4H^+(aq) \rightarrow 2Fe^{2+}(aq) + 2H_2O(l)$$
$$E^o = 1.67\ \text{V}$$

At $[Fe^{2+}] = 10^{-3}$ M, $p(O_2) = 0.1$ atm and pH = 3, the cell potential at 20°C is

(A) 1.47 V (B) 1.77 V
(C) 1.87 V (D) 1.57 V **(IIT-JEE 2011)**

Solution

(D) For the reaction

$$2Fe(s) + O_2(g) + 4H^+ \rightarrow 2Fe^{+2}(aq) + 2H_2O(l)$$
$$E^o = 1.67\ \text{V}$$

Using Nernst equation,

$$E_{cell} = E^o_{cell} - \left(\frac{0.0591}{n}\right)\log\frac{[Fe^{+2}]^2}{[O_2][H^+]^4}$$
$$= 1.67 - \left(\frac{0.0591}{4}\right)\log\frac{(10^{-3})^2}{(10^{-1})(10^{-3})^4}$$
$$= 1.67 - \left(\frac{0.0591}{4}\right)\log\frac{10^{-6}}{10^{-13}}$$
$$= 1.67 - \left(\frac{0.0591}{4}\right) \times 7 = 1.57\ \text{V}$$

11. Read the passage and answer the questions that follow: The electrochemical cell shown below is a concentration cell. $M|M^{2+}$ (saturated solution of a sparingly soluble salt, MX_2)$||M^{2+}$ (0.001 mol dm^{-3})|M

The emf of the cell depends on the difference in concentrations of M^{2+} ions at the two electrodes. The emf of the cell at 298 K is 0.059 V. **(IIT-JEE 2012)**

11a. The value of ΔG (kJ mol^{-1}) for the given cell is (take 1 F = 96500 C mol^{-1})

(A) –5.7 (B) 5.7
(C) 11.4 (D) –11.4

Solution

(D) At the anode: $M \rightarrow M^{2+} + 2e^-$
At the cathode: $M^{2+} + 2e^- \rightarrow M$
We know that $\Delta G = -nFE_{cell}$. Given that $E_{cell} = 0.059$ V, 1 F = 96500 C and n = number of electrons = 2. Substituting, we get

$$\Delta G = -2 \times 96500 \times 0.059 = -113873\ \text{J mol}^{-1}$$
$$= -11.387 = 11.4\ \text{kJ mol}^{-1}$$

11b. The solubility product (K_{sp}; $mol^3\ dm^{-9}$) of MX_2 at 298 K based on the information available for the given concentration cell is (take $2.303 \times R \times 298/F = 0.0591$ V).

(A) 1×10^{-15} (B) 4×10^{-15}
(C) 1×10^{-12} (D) 4×10^{-12}

Solution

(B) Using the Nernst equation at equilibrium

$$E_{\text{cell}} = -\frac{0.0591}{n}\log\frac{[\mathrm{M}^{2+}]^a}{[\mathrm{M}^{2+}]^c} = \frac{0.0591}{2}\log\frac{0.001}{[\mathrm{M}^{2+}]^a}$$

or $[\mathrm{M}^{2+}] = 10^{-5} = S$

From the equation

$$\underset{S}{\mathrm{MX}_2} \rightleftharpoons \underset{S}{\mathrm{M}^{2+}} + \underset{2S}{2\mathrm{X}^-}$$

Therefore, $K_{sp} = 4S^3 = 4 \times (10^{-5})^3 = 4 \times 10^{-15}\ \mathrm{mol^3\ dm^{-9}}$.

12. An aqueous solution of **X** is added slowly to an aqueous solution of **Y** as shown in **List I**. The variation in conductivity of these reactions is given in **List II**. Match **List I** with **List II** and select the correct answer using the code given below the lists:

List I	**List II**
P. $\underset{X}{(C_2H_5)_3N} + \underset{Y}{CH_3COOH}$	1. Conductivity decreases and then increases
Q. $\underset{X}{\mathrm{KI\ (0.1\ M)}} + \underset{Y}{\mathrm{AgNO_3\ (0.01\ M)}}$	2. Conductivity decreases and then does not change much
R. $\underset{X}{CH_3COOH} + \underset{Y}{KOH}$	3. Conductivity increases and then does not change much
S. $\underset{X}{NaOH} + \underset{Y}{HI}$	4. Conductivity does not change much and then increases

	P	**Q**	**R**	**S**
(A)	3	4	2	1
(B)	4	3	2	1
(C)	2	3	4	1
(D)	1	4	3	2

(JEE Advanced 2013)

Solution

(A) In the given reactions:

For (P): $\underset{X}{(C_2H_5)_3N} + \underset{Y}{CH_3COOH} \rightarrow (C_2H_5)_3\overset{+}{N}HCH_3COO^-$

First, the conductivity increases due to neutralization of CH_3COOH and replacement of H^+ by $(C_2H_5)_3\overset{+}{N}H$, after that it becomes practically constant due to buffering, because of which $[H^+]$ becomes constant and $[(C_2H_5)_3\overset{+}{N}H]$ increases.

For (Q): $\underset{X}{\mathrm{KI\ (0.1\ M)}} + \underset{Y}{\mathrm{AgNO_3\ (0.01\ M)}} \rightarrow \mathrm{AgI} + \mathrm{KNO_3}$

Initially, only Ag^+ is replaced by K^+, so the number of ions in the solution remains constant till all of $AgNO_3$ is precipitated as AgI. After this precipitation, conductance increases due to increase in number of ions

For (R): $\underset{X}{CH_3COOH} + \underset{Y}{KOH} \rightarrow CH_3COOK + H_2O$

Initially conductance decreases due to replacement of OH^- by CH_3COO^- and then slowly increases due to the increases in number of H^+ ions.

For (S): $\underset{X}{NaOH} + \underset{Y}{HI} \rightarrow NaI + H_2O$

Initially, conductance decreases due to replacement of H^+ ions by Na^+ and then increases due to the increase in OH^- ions.

13. The standard reduction potential data at 25°C is given below.

$$E^\circ(\mathrm{Fe^{3+}, Fe^{2+}}) = +0.77\ \mathrm{V};$$
$$E^\circ(\mathrm{Fe^{2+}, Fe}) = -0.44\ \mathrm{V}$$
$$E^\circ(\mathrm{Cu^{2+}, Cu}) = +0.34\ \mathrm{V};$$
$$E^\circ(\mathrm{Cu^{+}, Cu}) = +0.52\ \mathrm{V}$$
$$E^\circ[\mathrm{O_2(g)} + 4\mathrm{H^+} + 4e^- \rightarrow 2\mathrm{H_2O}] = +1.23\ \mathrm{V};$$
$$E^\circ[\mathrm{O_2(g)} + 2\,\mathrm{H_2O} + 4e^- \rightarrow 4\mathrm{OH^-}] = +0.40\ \mathrm{V}$$
$$E^\circ(\mathrm{Cr^{3+}, Cr}) = -0.74\ \mathrm{V};$$
$$E^\circ(\mathrm{Cr^{2+}, Cr}) = -0.91\ \mathrm{V}$$

Match E° of the redox pair in **List I** with the values given in **List II** and select the correct answer using the code given below the lists:

List I	**List II**
P. $E^\circ\ (\mathrm{Fe^{3+}, Fe})$	1. –0.18 V
Q. $E^\circ(4\mathrm{H_2O} \rightleftharpoons 4\mathrm{H^+} + 4\mathrm{OH^-})$	2. –0.4 V
R. $E^\circ(\mathrm{Cu^{2+} + Cu \rightarrow 2Cu^+})$	3. –0.04 V
S. $E^\circ(\mathrm{Cr^{3+}, Cr^{2+}})$	4. –0.83 V

	P	**Q**	**R**	**S**
(A)	4	1	2	3
(B)	2	3	4	1
(C)	1	2	3	4
(D)	3	4	1	2

(JEE Advanced 2013)

Solution

(D) In the given reactions.

For (P): The half reactions and net reactions are as follows:

$$\mathrm{Fe^{3+}} + e^- \rightarrow \mathrm{Fe^{2+}}$$
$$\underline{\mathrm{Fe^{2+}} + 2e^- \rightarrow \mathrm{Fe}}$$
$$\mathrm{Fe^{3+}} + 3e^- \rightarrow \mathrm{Fe}$$

For the overall reaction,

$$\Delta G_3^\circ = \Delta G_1^\circ + \Delta G_2^\circ$$
$$-3F \times E^\circ_{\mathrm{Fe^{3+}/Fe}} = -1F \times 0.77 - 2F \times (-0.44)$$

Solving, we get

$$3E^{\circ}_{Fe^{3+}/Fe} = -0.11 \Rightarrow E^{\circ}_{Fe^{3+}/Fe} = -\frac{0.11}{3} =$$

$$-0.036\ V \approx -0.04\ V$$

For (Q): The half reactions and net reactions are as follows:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad E^{\circ} = -1.23\,V$$
$$\underline{4e^- + O_2 + 2H_2O \rightarrow OH^- \quad E^{\circ} = 0.40\,V}$$
$$4H_2O \rightarrow 4H^+ + 4OH^- \quad E^{\circ} = ?$$

For the overall reaction, $E^{\circ} = -1.23 + 0.40 = -0.83$ V

For (R): The half reactions and net reactions are as follows:

$$Cu^{2+} + 2e^- \rightarrow Cu \quad E^{\circ} = +0.34\,V$$
$$\underline{2Cu \rightarrow Cu^+ + 2e^- \quad E^{\circ} = -0.52\,V}$$
$$Cu^{2+} + Cu \rightarrow 2Cu^+ \quad E^{\circ} = ?$$

For the overall reaction, $E^{\circ} = 0.34 - 0.52 = -0.18$ V

For (S): The half reactions and net reactions are as follows:

$$Cr^{3+} + 3e^- \rightarrow Cr$$
$$\underline{Cr \rightarrow Cr^{2+} + 2e^-}$$
$$Cr^{3+} + e^- \rightarrow Cr^{2+}$$

For the overall reaction,

$$\Delta G^{\circ}_3 = \Delta G^{\circ}_1 + \Delta G^{\circ}_2$$
$$-1F \times E^{\circ}_{Cr^{3+}/Cr^{2+}} = 3F \times 0.74 - 2F \times 0.91$$

Solving, we get $E^{\circ}_{Cr^{3+}/Cr^{2+}} = -0.4$ V

14. In a galvanic cell, the salt bridge

(A) does not participate chemically in the cell reaction.
(B) stops the diffusion of ions from one electrode to another.
(C) is necessary for the occurrence of the cell reaction.
(D) ensures mixing of the two electrolytic solutions.

(JEE Advanced 2014)

Solution

(A) The salt bridge contains neutral electrolyte and hence does not participate in the reaction.

15. All the energy released from the reaction **X** → **Y**, $\Delta_r G^0 = -193$ kJ mol^{-1} is used for oxidizing $\mathbf{M}^+$ as $\mathbf{M}^+ \rightarrow \mathbf{M}^{3+} + 2e^-$, $E^0 = -0.25$ V.

Under standard conditions, the number of moles of $\mathbf{M}^+$ oxidized when one mole of X is converted to Y is _____.

[$F = 96500$ C mol^{-1}] **(JEE Advanced 2015)**

Solution

(4) We know that

$$\Delta G^0 = -nFE^0_{cell}$$
$$= -2 \times 96{,}500 \times (-0.25)$$
$$= 48{,}250\,J = 48.25\,kJ$$

For energy conversion of one mole of $M^+ \rightarrow M^{3+}$, the requirement is 48.25 kJ.

Therefore, with 193 kJ, number of moles of M oxidized is equal to 193/48.25 = 4 mol

16. The molar conductivity of a solution of a weak acid HX (0.01 M) is 10 times smaller than the molar conductivity of a solution of a weak acid HY (0.10 M). If $\lambda^0_{X^-} \approx \lambda^0_{Y^-}$, the difference in their pK_a values, pK_a(HX) – pK_a(HY), is _________.

(consider degree of ionization of both acids to be $\ll$1)

(JEE Advanced 2015)

Solution

(3) For HX and HY since $\lambda^0_{X^-} \approx \lambda^0_{Y^-}$,

$$\frac{\lambda_C(HX)}{\lambda_C(HY)} = \frac{\alpha_{HX}}{\alpha_{HY}} = \frac{1}{10}$$

$$\frac{H^+_{(HX)}}{H^+_{(HY)}} = \frac{(C\alpha)_{HX}}{(C\alpha)_{HY}} = \frac{\sqrt{(K_aC)_{HX}}}{\sqrt{(K_aC)_{HY}}} \qquad (1)$$

$$\frac{H^+_{(HX)}}{H^+_{(HY)}} \approx \frac{0.01}{0.1} \times \frac{1}{10} = 1$$

Taking negative log of both the sides of Eq. (1), we get

$$pH(HX) - pH(HY) = -\frac{1}{2}\log(K_aC)_{HX} - \left[-\frac{1}{2}\log(K_aC)_{HY}\right]$$
$$0 = \frac{1}{2}[pK_a(HX) - 2] - \frac{1}{2}[pK_a(HY) - 1]$$
$$0 = pK_a(HX) - pK_a(HY) - 3$$
$$\Rightarrow pK_a(HX) - pK_a(HY) = 3$$

17. When during electrolysis of a solution of $AgNO_3$, 9650 C of charge pass through the electroplating bath, the mass of silver deposited on the cathode will be **(AIEEE 2003)**

(A) 1.08 g	(B) 10.8 g
(C) 21.6 g	(D) 108 g

Solution

(B) 1 F of charge is required to deposit 108 g of silver.
96500 C of charge is required to deposit 108 g of silver.

$$9650\text{ C will deposit } \frac{108}{96500} \times 9650 = 10.8\text{ g silver.}$$

18. For the redox reaction: $Zn(s) + Cu^{2+}(0.1\,M) \rightarrow Zn^{2+}(1\,M) + Cu(s)$ taking place in a cell, E°_{cell} is 1.10 V. E_{cell} for the cell will be [2.303 (RT/F) = 0.0591] **(AIEEE 2003)**

(A) 2.14 V	(B) 1.80 V
(C) 1.07 V	(D) 0.82 V

Solution

(C) According to Nernst equation, at STP we have

$$E_{\text{cell}} = E^{\text{o}}_{\text{cell}} - \frac{0.0591}{n}\log\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$
$$= 1.1 - \frac{0.0591}{2}\log\frac{1}{0.1} = 1.07 \text{ V}$$

19. For a cell reaction involving a two–electron change, the standard emf of the cell is found to be 0.295 V at 25°C. The equilibrium constant of the reaction at 25°C will be **(AIEEE 2003)**

(A) 1×10^{-10} (B) 29.5×10^{-2}
(C) 10 (D) 1×10^{10}

Solution

(D) We know that $E^{\text{o}}_{\text{cell}} = \dfrac{0.0591}{n}\log K_C$. Given that $n = 2$, so we have

$$K_C = \text{antilog}\left(\frac{2\times 0.295}{0.0591}\right) = 1\times 10^{10}$$

20. Standard reduction electrode potentials of three metals A, B and C are, respectively, +0.5 V, −3.0 V and −1.2 V. The reducing powers of these metals are **(AIEEE 2003)**

(A) B > C > A (B) A > B > C
(C) C > B > A (D) A > C > B

Solution

(A) Higher the value of reduction potential, stronger is the oxidizing agent.

21. Several blocks of magnesium are fixed to the bottom of a ship to **(AIEEE 2003)**

(A) keep away the sharks.
(B) make the ship lighter.
(C) prevent action of water and salt.
(D) prevent puncturing by under sea rocks.

Solution

(C) This is done to prevent corrosion caused by water and salt.

22. In hydrogen–oxygen fuel cell, combustion of hydrogen occurs to **(AIEEE 2004)**

(A) generate heat.
(B) remove adsorbed oxygen from electrode surfaces.
(C) produce high purity water.
(D) create potential difference between the two electrodes.

Solution

(D) By creating potential difference between two electrodes, fuel cell can be used to generate electricity.

23. Consider the following E^{o} values, $E^{\text{o}}_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.77$ V and $E^{\text{o}}_{\text{Sn}^{2+}/\text{Sn}} = -0.14$ V. Under standard conditions is the potential for the reaction is $\text{Sn(s)} + 2\text{Fe}^{3+}\text{(aq)} \rightarrow 2\text{Fe}^{2+}\text{(aq)} + \text{Sn}^{2+}\text{ (aq)}$

(A) 1.68 V (B) 0.63 V
(C) 0.91 V (D) 1.40 V **(AIEEE 2004)**

Solution

(C) At the cathode: $\text{Fe}^{3+}\text{(aq)} + e^- \rightarrow \text{Fe}^{2+}\text{(aq)}$

At the anode: $\text{Sn(s)} \rightarrow \text{Sn}^{2+}\text{(aq)} + 2e^-$

$$E^{\text{o}}_{\text{cell}} = E^{\text{o}}_{\text{cathode}} - E^{\text{o}}_{\text{anode}} = 0.77 - (-0.14) = 0.91 \text{ V}$$

24. The standard emf of a cell, involving one electron charge is found to be 0.591 V at 25°C. The equilibrium constant of the reaction is (F = 96,500 C mol^{-1}: R = 8.314 J K^{-1} mol^{-1}) **(AIEEE 2004)**

(A) 1.0×10^{1} (B) 1.0×10^{30}
(C) 1.0×10^{10} (D) 1.0×10^{5}

Solution

(C) We have $E^{\text{o}}_{\text{cell}} = \dfrac{0.0591}{n}\log K_C$, so $\log K_C = \dfrac{1\times 0.591}{0.0591} = 10$

or $$K_C = 1\times 10^{10}$$

25. The limiting molar conductivities Λ^0 for NaCl, KBr and KCl are 126, 152 and 150 S cm^2 mol^{-1}, respectively. The Λ^0 for NaBr is **(AIEEE 2004)**

(A) 128 S cm^2 mol^{-1} (B) 302 S cm^2 mol^{-1}
(C) 278 S cm^2 mol^{-1} (D) 176 S cm^2 mol^{-1}

Solution

(A) $$\Lambda^0_{(\text{NaBr})} = \Lambda^0_{(\text{NaCl})} + \Lambda^0_{(\text{KBr})} - \Lambda^0_{(\text{KCl})}$$
$$= 126 + 152 - 150 = 128 \text{ S cm}^2\text{ mol}^{-1}$$

26. The $E^{\text{o}}_{\text{M}^{+3}/\text{M}^{2+}}$ values for Cr, Mn, Fe and Co are –0.41, +1.57, +0.77 and +1.97 V, respectively. For which one of these metals the change in oxidation state from +2 to +3 is the easiest? **(AIEEE 2004)**

(A) Cr (B) Co
(C) Fe (D) Mn

Solution

(A) Changing oxidation number from +2 to +3 means undergoing oxidation. As we know that from the reactivity series, metals with lower E^{o} values undergo oxidation easily than those with higher E^{o} values.

27. During the process of electrolytic refining of copper, some metals present as impurity settle as “anode mud”. These are **(AIEEE 2005)**

(A) Sn and Ag (B) Pb and Zn
(C) Ag and Au (D) Fe and Ni

Solution

(C) The electrolytic method contains valuable metals in the form of anode mud, that is, silver and gold.

28. The highest electrical conductivity of the following aqueous solutions is of **(AIEEE 2005)**

(A) 0.1 M acetic acid.
(B) 0.1 M chloroacetic acid.
(C) 0.1 M fluoroacetic acid.
(D) 0.1 M difluoroacetic acid.

Solution

(D) This is because the electrical conductivity depends on the strength of the acid, and difluoroacetic acid is the strongest among these.

29. Aluminium oxide may be electrolyzed at 1000°C to furnish aluminium metal (atomic mass = 27 amu; 1 F = 96,500 C). The cathode reaction is $Al^{3+} + 3e^- \rightarrow Al^0$. To prepare 5.12 kg of aluminium metal by this method would require **(AIEEE 2005)**

(A) 5.49×10^7 C of electricity
(B) 1.83×10^7 C of electricity
(C) 5.49×10^4 C of electricity
(D) 5.49×10^1 C of electricity

Solution

(A) To prepare 27 g of Al, electricity required = $3F = 3 \times 96500$ C

Therefore, 5.12 kg (5120 g) will require

$$\frac{3 \times 96500 \times 5120}{27} = 5.49 \times 10^7 \text{ C}$$

30. The molar conductivities Λ^0_{NaOAc} and Λ^0_{HCl} at infinite dilution in water at 25°C are 91.0 and 426.2 S cm^2 mol^{-1}, respectively. To calculate Λ^0_{HOAc}, the additional value required is **(AIEEE 2006)**

(A) $\Lambda^0_{H_2O}$
(B) Λ^0_{KCl}
(C) Λ^0_{NaOH}
(D) Λ^0_{NaCl}

Solution

(D) According to Kohlrausch's law,

$$\Lambda^0_{CH_3COONa} = \lambda^0_{CH_3COO^-} + \lambda^0_{Na^+} \quad (1)$$

$$\Lambda^0_{HCl} = \lambda^0_{H^+} + \lambda^0_{Cl^-} \quad (2)$$

$$\Lambda^0_{NaCl} = \lambda^0_{Na^+} + \lambda^0_{Cl^-} \quad (3)$$

Adding Eqs. (1) and (2) and subtracting Eq. (3) from the sum, we get

$$\Lambda^0_{CH_3COOH} = \lambda^0_{CH_3COO^-} + \lambda^0_{H^+} = \Lambda^0_{CH_3COONa} + \Lambda^0_{HCl} - \Lambda^0_{NaCl}$$

31. Given the data at 25°C,

$$Ag + I^- \rightarrow AgI + e^-; \quad E^\circ = 0.152 \text{ V}$$

$$Ag \rightarrow Ag^+ + e^-; \quad E^\circ = -0.800 \text{ V}$$

What is the value of log K_{sp} for AgI? **(AIEEE 2006)**

(A) –8.12
(B) +8.612
(C) –37.83
(D) –16.13

Solution

(D) Reversing the first reaction and adding to the second

$$AgI(s) + e^- \rightarrow Ag(s) + I^-(aq); \quad E^\circ = -0.152 \text{ V}$$

$$Ag(s) \rightarrow Ag^+(aq) + e^-; \quad E^\circ = -0.800 \text{ V}$$

we get $AgI(s) \rightarrow Ag^+(aq) + I^-(aq) \quad E^\circ = -0.952 \text{ V}$

Now, $E^\circ_{cell} = \dfrac{2.303RT}{nF}\log K_{sp}$. Substituting values, we get

$$-0.952 = \frac{0.059}{1}\log K_{sp}$$

or

$$\log K_{sp} = -\frac{0.952}{0.059} = -16.135$$

32. Resistance of a conductivity cell filled with a solution of an electrolyte of concentration 0.1 M is 100 Ω. The conductivity of this solution is 1.29 S m^{-1}. Resistance of the same cell when filled with 0.2 M of the same solution is 520 Ω. The molar conductivity of 0.02 M solution of the electrolyte will be **(AIEEE 2006)**

(A) 124×10^{-4} S m^2 mol^{-1}
(B) 1240×10^{-4} S m^2 mol^{-1}
(C) 1.24×10^{-4} S m^2 mol^{-1}
(D) 12.4×10^{-4} S m^2 mol^{-1}

Solution

(D) Given that R = 100 Ω. Now, specific conductance is

$$\kappa = \frac{1}{R}\left(\frac{l}{a}\right) \Rightarrow 1.29 = \frac{1}{100}\left(\frac{l}{a}\right) \Rightarrow \frac{l}{a} = 129 \text{ m}^{-1}$$

When $R = 520$ Ω, C = 0.2 M we have

$$\kappa = \frac{1}{R}\left(\frac{l}{a}\right) = \frac{1}{520}(129) \text{ S m}^{-1}$$

Now, molar conductivity (Λ_m) is $\Lambda_m = \kappa \times V$ where V is in cm^3. Now, if M is concentration of solution in mol L^{-1}, then

$$\Lambda_m = \kappa \times \frac{1000}{M} = \frac{1}{520} \times 129 \times \frac{1000}{0.2} \times 10^{-6}$$
$$= 1.24 \times 10^{-3} = 12.4 \times 10^{-4} \text{ S m}^2\text{mol}^{-1}$$

33. The equivalent conductances of two strong electrolytes at infinite dilution in H_2O (where ions move freely through a solution) at 25°C are $\Lambda^0_{CH_3COONa} = 91.0$ S cm^{2}equiv^{-1} and $\Lambda^0_{HCl} = 426.2$ S cm^{2}equiv^{-1}. What additional information/quantity is needed to calculate Λ^0 of an aqueous solution of acetic acid?

(A) Λ^0 of chloroacetic acid ($ClCH_2COOH$)
(B) Λ^0 of NaCl
(C) Λ^0 of CH_3COOK
(D) The limiting equivalent conductance of $H^+ (\lambda^0_{H^+})$

(AIEEE 2007)

Solution

(B) From Kohlrausch's law,

$$\Lambda^0_{CH_3COOH} = \Lambda^0_{CH_3COONa} + \Lambda^0_{HCl} - \Lambda^0_{NaCl}$$

34. The cell, $Zn|Zn^{2+}(1\text{ M}) \,||\, Cu^{2+}(1\text{ M}) \,|\, Cu$ ($E^\circ_{cell} = 1.10$ V), was allowed to be completely discharged at 298 K. The relative concentration of Zn^{2+} to Cu^{2+}, that is, $[Zn^{2+}]/[Cu^{2+}]$ is

(A) 9.65×10^4
(B) antilog (24.08)
(C) 37.3
(D) 1.995×10^{37}

(AIEEE 2007)

Solution

(D) Using Nernst equation, $E_{cell} = E^\circ_{cell} - \dfrac{0.0591}{n}\log\dfrac{[Zn^{2+}]}{[Cu^{2+}]}$

For complete discharge, $E_{\text{cell}} = 0$. So,

$$E^{\text{o}}_{\text{cell}} - \frac{0.0591}{n}\log\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} = 0$$

The reactions are

$$\text{Zn(s)} \rightarrow \text{Zn}^{2+}\text{(aq)} + 2e^-$$

$$\text{Cu}^{2+}\text{(s)} + 2e^- \rightarrow \text{Cu(s)}$$

So for $n = 2$, $E^{\text{o}}_{\text{cell}} = \frac{0.0591}{2}\log\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$

Solving, we get $E^{\text{o}}_{\text{cell}} = 1.10$ V (given), so

$$\frac{1.10\times 2}{0.0591} = \log\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

$$37.3 = \log\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \Rightarrow \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} = 1.995\times 10^{37}$$

35. Given $E^{\text{o}}_{\text{Cr}^{3+}/\text{Cr}} = -0.72$ V, $E^{\text{o}}_{\text{Fe}^{2+}/\text{Fe}} = -0.42$ V. The potential for the cell $\text{Cr}\,|\,\text{Cr}^{3+}(0.1\text{ M})\,||\,\text{Fe}^{2+}(0.01\text{ M})\,|\,\text{Fe}$ is

(A) 0.26 V (B) 0.399 V
(C) –0.339 V (D) –0.26 V

(AIEEE 2008)

Solution

(A) Given that $E^{\text{o}}_{\text{Cr/Cr}^{3+}} = -0.72$ V and $E^{\text{o}}_{\text{Fe}^{2+}/\text{Fe}} = -0.42$ V. For the reaction $2\text{Cr(s)} + 3\text{Fe}^{2+}\text{(aq)} \rightarrow 3\text{Fe(s)} + 2\text{Cr}^{3+}\text{(aq)}$, according to Nernst equation

$$E_{\text{cell}} = E^{\text{o}}_{\text{cell}} - \frac{0.0591}{n}\log\frac{[\text{Cr}^{3+}]^2}{[\text{Fe}^{2+}]^3}$$

$$= (-0.42 + 0.72) - \frac{0.0591}{6}\log\frac{(0.1)^2}{(0.01)^3}$$

$$= 0.30 - \frac{0.0591}{6}\log\frac{(0.1)^2}{(0.01)^3}$$

$$= 0.30 - \frac{0.0591}{6}\log\frac{10^{-2}}{10^{-6}} = 0.30 - \frac{0.0591}{6}\log 10^4$$

$$= 0.30 - 0.0394 = 0.2606\text{ V}$$

36. Given that $E^{\text{o}}_{\text{Fe}^{3+}/\text{Fe}} = -0.036$ V, $E^{\text{o}}_{\text{Fe}^{2+}/\text{Fe}} = -0.439$ V. The value of standard electrode potential for the change, $\text{Fe}^{3+}\text{(aq)} + e^- \rightarrow \text{Fe}^{2+}\text{(aq)}$ will be:

(A) 0.770 V (B) –0.270 V
(C) –0.072 V (D) 0.385 V

(AIEEE 2009)

Solution

(A) For the reaction

$$\text{Fe}^{3+}\text{(aq)} + 3e^- \rightarrow \text{Fe(s)};\quad E^{\text{o}} = -0.036\text{ V} \qquad (1)$$

The Gibbs energy is given by

$$\Delta G^{\text{o}}_1 = -nFE^{\text{o}} = -3\times F\times(-0.036) = +0.108\ F$$

For the reaction

$$\text{Fe}^{2+}\text{(aq)} + 2e^- \rightarrow \text{Fe(s)};\quad E^{\text{o}} = -0.439\text{ V}$$

or $\quad \text{Fe(s)} \rightarrow \text{Fe}^{2+}\text{(aq)} + 2e^-;\quad E^{\text{o}} = 0.439\text{ V} \qquad (2)$

The Gibbs energy is given by

$$\Delta G^{\text{o}}_2 = -nFE^{\text{o}} = -2F(0.439) = -0.878\ F$$

For the reaction $\text{Fe}^{3+}\text{(aq)} + e^- \rightarrow \text{Fe}^{2+}\text{(aq)}$. The Gibbs energy is given by

$$\Delta G^{\text{o}} = -nFE^{\text{o}} = -1FE^{\text{o}} \qquad (3)$$

Equation (3) can be obtained by adding Eqs. (1) and (2), therefore

$$\Delta G^{\text{o}} = \Delta G^{\text{o}}_1 + \Delta G^{\text{o}}_2$$

$$-FE^{\text{o}} = 0.108F + (-0.878)F = -0.77F$$

or $\quad E^{\text{o}} = 0.77$ V

37. In a fuel cell, methanol is used as fuel and oxygen gas is used as an oxidizer. The reaction is

$$\text{CH}_3\text{OH(l)} + \tfrac{3}{2}\text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)} + 2\text{H}_2\text{O(l)}$$

At 298 K, standard Gibbs' energies of formation for CH_3OH (l), H_2O (l) and CO_2 (g) are –166.2 kJ mol^{-1}, –237.2 kJ mol^{-1} and –394.4 kJ mol^{-1}, respectively. If standard enthalpy of combustion of methanol is –726 kJ mol^{-1}, efficiency of the fuel cell will be

(A) 90% (B) 97%
(C) 80% (D) 87%

(AIEEE 2009)

Solution

(B) For the reaction,

$$\text{CH}_3\text{OH(l)} + \tfrac{3}{2}\text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)} + 2\text{H}_2\text{O(l)},$$

$$\Delta G = \Delta G^\circ(\text{CO}_2) + 2\Delta G^\circ(\text{H}_2\text{O}) - \Delta G^\circ(\text{CH}_3\text{OH})$$

$$= -394 - 2(237.2) + 166.2 = -702.6\text{ kJ mol}^{-1}$$

Efficiency of fuel cell is $\frac{\Delta G}{\Delta H}\times 100 = \frac{702.6}{726}\times 100 = 97\%$

38. The Gibbs energy for the decomposition of Al_2O_3 at 500°C is as follows:

$$\tfrac{2}{3}\text{Al}_2\text{O}_3 \rightarrow \tfrac{4}{3}\text{Al} + \text{O}_2,\quad \Delta_r G = +966\text{ kJ mol}^{-1}$$

The potential difference needed for electrolytic reduction of Al_2O_3 at 500°C is at least

(A) 5.0 V (B) 4.5 V
(C) 3.0 V (D) 2.5 V

(AIEEE 2010)

Solution

(D) From the relation $\Delta G = -nFE$, we have

$$E = -\frac{\Delta G}{nF} = -\frac{966\times 10^3}{4\times 96{,}500} = -2.5\text{ V (for oxidation)}$$

Therefore, potential difference needed for reduction = $-E$ (oxidation) = 2.5 V

39. The reduction potential of hydrogen half-cell will be negative if:

(A) $p(H_2) = 1$ atm and $[H^+] = 1.0$ M
(B) $p(H_2) = 2$ atm and $[H^+] = 1.0$ M
(C) $p(H_2) = 2$ atm and $[H^+] = 2.0$ M
(D) $p(H_2) = 1$ atm and $[H^+] = 2.0$ M

(AIEEE 2011)

Solution

(B) The reaction is: $2H^+(aq) + 2e^- \rightarrow H_2(g)$

$$E = E^o - 0.059\log\left(\frac{p(H_2)}{[H^+]^2}\right)$$

$$= -\frac{0.0591}{2} \times 0.3010 = \text{Negative value}$$

E is negative only when $p(H_2) > [H^+]^2$.

40. The standard reduction potentials for Zn^{2+}/Zn, Ni^{2+}/Ni, and Fe^{2+}/Fe are –0.76 V, –0.23 V and –0.44 V, respectively. The reaction $X + Y^{2+} \rightarrow X^{2+} + Y$ will be spontaneous when

(AIEEE 2012)

(A) X = Ni, Y = Fe
(B) X = Ni, Y = Zn
(C) X = Fe, Y = Zn
(D) X = Zn, Y = Ni

Solution

(D) Looking at the standard reduction potentials, it is clear that Zn is the strongest reducing agent and Ni is the weakest reducing agent. So, Zn will displace both Ni and Fe. Fe will displace only Ni and not Zn as Zn is a stronger reducing agent; while Ni will not displace either Zn or Fe as it is the weakest reducing agent

$$Zn(s) + Fe^{2+}(aq) \rightarrow Zn^{2+}(aq) + Fe(s)$$
$$Fe(s) + Ni^{2+}(aq) \rightarrow Fe^{2+}(aq) + Ni(s)$$
$$Zn(s) + Ni^{2+}(aq) \rightarrow Zn^{2+}(aq) + Ni(s)$$

41. Four successive members of the first row transition elements are listed below with atomic numbers. Which one of them is expected to have the highest $E^o_{M^{3+}/M^{2+}}$ value?

(A) Mn ($Z = 25$)
(B) Fe ($Z = 26$)
(C) Co ($Z = 27$)
(D) Cr ($Z = 24$)

(JEE Main 2013)

Solution

(C) We know that

$$E^o_{Mn^{3+}/Mn^{2+}} = 1.57\text{ V},\ E^o_{Fe^{3+}/Fe^{2+}} = 0.77\text{ V}$$
$$E^o_{Co^{3+}/Co^{2+}} = 1.97\text{ V and } E^o_{Cr^{3+}/Cr^{2+}} = -0.41\text{ V}$$

42. Given $E^o_{Cr^{3+}/Cr} = -0.74\text{ V}; E^o_{MnO_4^-/Mn^{2+}} = 1.51\text{ V}, E^o_{Cr_2O_7^{2-}/Cr^{3+}} = 1.33\text{ V}; E^o_{Cl/Cl^-} = 1.36\text{ V}$ Based on the data given above, strongest oxidizing agent will be

(A) Cr^{3+}
(B) Mn^{2+}
(C) MnO_4^-
(D) Cl^-

(JEE Main 2013)

Solution

(C) As per the data given, MnO_4^- is the strongest oxidizing agent as it has maximum standard reduction potential (SRP) value.

The values of SRP are

$$E^o_{Cr^{3+}/Cr} = -0.74\text{ V};\ E^o_{MnO_4^-/Mn} = 1.51\text{ V};$$
$$E^o_{Cr_2O_7^{2-}/Cr^{3+}} = 1.33\text{ V};\ E^o_{Cl/Cl^-} = 1.36\text{ V}$$

On the basis of given data correct order of oxidizing behavior is: $MnO_4^- > Cl > Cr_2O_7^{2-} > Cr^{3+}$

43. The equivalent conductance of NaCl at concentration C and at infinite dilution is λ_C and λ_∞, respectively. The correct relationship between λ_C and λ_∞ is given as (where the constant B is positive)

(A) $\lambda_C = \lambda_\infty + (B)C$
(B) $\lambda_C = \lambda_\infty - (B)C$
(C) $\lambda_C = \lambda_\infty - (B)\sqrt{C}$
(D) $\lambda_C = \lambda_\infty + (B)\sqrt{C}$

(JEE Main 2014)

Solution

(C) According to Debye–Huckle–Onsager equation,

$$\lambda_C = \lambda_\infty - B\sqrt{C}.$$

44. Given below are the half-cell reactions

$$Mn^{2+} + 2e^- \rightarrow Mn; \quad E^o = -1.18\text{ V}$$
$$2(Mn^{3+} + e^- \rightarrow Mn^{2+}); \quad E^o = +1.51\text{ V}$$

The E^o for $3Mn^{2+} \rightarrow Mn + 2Mn^{3+}$ will be

(A) –2.69 V; the reaction will not occur.
(B) –2.69 V; the reaction will occur.
(C) –0.33 V; the reaction will not occur.
(D) –0.33 V; the reaction will occur.

(JEE Main 2014)

Solution

(A) Given that

$$Mn^{2+} + 2e^- \rightleftharpoons Mn; \qquad E^o = -1.18\text{ V} \qquad (1)$$
$$[Mn^{3+} + e^- \rightleftharpoons Mn^{2+}] \times 2;\ E^o = +1.51\text{ V} \qquad (2)$$
$$[Mn^{2+} \rightleftharpoons Mn^{3+} + e^-] \times 2;\ E^o = -1.51\text{ V} \qquad (3)$$

Adding Eq. (1) by Eq. (3), we get

$$3Mn^{2+} \rightleftharpoons Mn + 2Mn^{3+}$$

for which $E^o = -1.18 - 1.51 = -2.69$ V

Negative electrode potential implies that disproportion is not spontaneous for Mn with +2 oxidation state to 0 and +3 oxidation states.

45. Two faraday of electricity is passed through a solution of $CuSO_4$. The mass of copper deposited at the cathode is: (At. mass of Cu = 63.5 amu)

(A) 63.5 g
(B) 2 g
(C) 127 g
(D) 0 g

(JEE Main 2015)

Solution

(A) According to Faraday's law of electrolysis and according to the reaction,

$$\mathrm{Cu^{2+} + 2\mathit{e}^- \rightarrow Cu}$$

2F will deposit 63.5 g of Cu.

REVIEW QUESTIONS

1. If $E^{\circ}_{\mathrm{Cu^{2-}}}$ had been chosen as the standard reference electrode and had been assigned a potential of 0.00 V, what would the reduction potential of the hydrogen electrode be relative to it?

2. What is a concentration cell? Why is the $E^{\circ}_{\mathrm{Cu^{2-}}}$ for such a cell equal to zero?

3. Why must electrolysis reactions occur at the electrodes in order for electrolytic conduction to continue?

4. Using the same current, which will require the greater length of time, depositing 0.10 mol Cu from a $\mathrm{Cu^{2+}}$solution, or depositing 0.10 mol of Cr from a $\mathrm{Cr^{3+}}$ solution? Explain your reasoning.

5. Molar conductance of an acetic acid solution increases drastically with dilution. Explain.

6. Electrolytic conductivity decreases with dilution. Explain.

7. An electric current is passed through two electrolysis cells connected in series (so the same amount of current passes through each of them). One cell contains $\mathrm{Cu^{2+}}$ and the other contains $\mathrm{Fe^{2+}}$. In which cell will the greater mass of metal be deposited? Explain your answer.

8. Explain the following:
   (a) The emf of a lead storage battery is dependent on concentration of sulphuric acid.
   (b) In primary alkaline cells, the electrolyte KOH is invariant.

9. How is hydrogen held as a reactant in a nickel–metal hydride battery? Write the chemical formula for a typical alloy used in this battery. What is the electrolyte?

10. Give two reasons why lithium is such an attractive anode material for use in a battery. What are the problems associated with using lithium for this purpose?

11. What advantages do fuel cells offer over conventional means of obtaining electrical power by the combustion of fuels?

12. Describe the electrolysis of aqueous sodium chloride. How do the products of the electrolysis compare for stirred and unstirred reactions? Write chemical equations for the reactions that occur at the electrodes.

13. What will be the spontaneous reaction among $\mathrm{Br_2}$, $\mathrm{I_2}$, $\mathrm{Br^-}$ and $\mathrm{I^-}$?

14. Write the cell notation for the following galvanic cells. For half-reactions in which all the reactants are in solution or are gases, assume the use of inert platinum electrodes.
   (a) $\mathrm{Cd^{2+}(aq) + Fe(s) \rightarrow Cd(s) + Fe^{2+}(aq)}$
   (b) $\mathrm{NiO_2(s) + 4H^+(aq) + 2Ag(s) \rightarrow Ni^{2+}(aq) + 2H_2O + 2Ag^+(aq)}$
   (c) $\mathrm{Mg(s) + Cd^{2+}(aq) \rightarrow Mg^{2+}(aq) + Cd(s)}$

15. From the half-reactions below, determine the cell reaction and standard cell potential.

$$\mathrm{BrO_3^- + 6H^+ + 6\mathit{e}^- \rightleftharpoons Br^- + 3H_2O}; \quad E^{\circ}_{\mathrm{BrO_3^-}} = 1.44\ \mathrm{V}$$

$$\mathrm{I_2 + 2\mathit{e}^- \rightleftharpoons 2I^-}; \quad E^{\circ}_{\mathrm{I_2}} = 0.54\ \mathrm{V}$$

16. What will be the spontaneous reaction among $\mathrm{H_2SO_3}$, $\mathrm{S_2O_3^{2-}}$, HOCl and $\mathrm{Cl_2}$? The half-reactions involved are

$$\mathrm{2H_2SO_3 + 2H^+ + 4\mathit{e}^- \rightleftharpoons S_2O_3{}^{2-} + 3H_2O}; \quad E^{\circ}_{\mathrm{H_2SO_3}} = 0.40\ \mathrm{V}$$

$$\mathrm{2HOCl + 2H^+ + 2\mathit{e}^- \rightleftharpoons Cl_2 + 2H_2O}; \quad E^{\circ}_{\mathrm{HOCl}} = 1.63\ \mathrm{V}$$

17. Explain why:
   (a) Nickel spatula cannot be used to stir copper sulphate solution.
   (b) Blue color of copper sulphate fades when electrolyzed using platinum electrode.

18. Given that the standard electrode potentials: $\mathrm{K^+/K} = -2.93$ V, $\mathrm{Ag^+/Ag} = 0.80$ V, $\mathrm{Cu^{2+}/Cu} = 0.34$ V, $\mathrm{Mg^{2+}/Mg} = -2.37$ V, $\mathrm{Cr^{3+}/Cr} = -0.74$ V, $\mathrm{Fe^{2+}/Fe} = -0.44$ V. Arrange these metals in the increasing order of their reducing power.

19. What do the positive and negative signs of reduction potentials tell us?

20. Why do electrochemical cells stop working after sometime?

21. In a concentration cell, give reasons for the following:
   (a) The cell potential doubles when concentration ratio is changed from 0.0001 to 0.01.
   (b) No electricity flows when the metal ion concentration at the two electrodes is the same.

22. What is the effect of dilution on
   (a) specific conductivity.
   (b) equivalent conductance of weak electrolytes.
   (c) equivalent conductance of strong electrolytes.

23. Predict the products of electrolysis in each of the following:
   (a) An aqueous solution of $\mathrm{AgNO_3}$ with silver electrodes.
   (b) An aqueous solution of $\mathrm{AgNO_3}$ with platinum electrodes.
   (c) A dilute solution of $\mathrm{H_2SO_4}$ with platinum electrodes.
   (d) An aqueous solution of $\mathrm{CuCl_2}$ with platinum electrodes.

24. What happens to the pH of the solution near the cathode and anode during the electrolysis of K_2SO_4? What function does K_2SO_4 serve in the electrolysis of a K_2SO_4 solution?

25. Why must NaCl be melted before it is electrolyzed to give Na and Cl_2? Write the anode, cathode and overall cell reactions for the electrolysis of molten NaCl.

26. **(a)** Why does dry cell become dead after sometime even if it has not been used?

(b) What is the role of $ZnCl_2$ in a dry cell?

27. Why a mercury cell gives a constant voltage throughout its life?

NUMERICAL PROBLEMS

1. Calculate ΔG° for the following reaction as written:

$$2Br^- + I_2 \rightarrow 2I^- + Br_2$$

2. Calculate ΔG° for the reaction

$$2MnO_4^- + 6H^+ + 5HCHO_2 \rightarrow 2Mn^{2+} + 8H_2O + 5CO_2$$

for which $E^\circ_{cell} = 1.69$ V

3. The system $2AgI + Sn \rightleftharpoons Sn^{2+} + 2Ag + 2I^-$ has a calculated E°_{cell} of –0.015 V. What is the value of K_C for this system?

4. The E°_{cell} is 0.135 V for the reaction

$3I_2(s) + 5Cr_2O_7^{2-}(aq) + 34H^+ \rightarrow 6IO_3^-(aq) + 10Cr^{3+}(aq) + 17H_2O$.

What is E_{cell} if $[Cr_2O_7^{2-}] = 0.010$ M, $[H^+] = 0.10$ M, $[IO_3^-] = 0.00010$ M, and $[Cr^{3+}] = 0.0010$ M?

5. A silver wire coated with AgCl is sensitive to the presence of chloride ion because of the half-cell reaction

$$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-(aq) \qquad E^\circ_{AgCl} = 0.2223 \text{ V}$$

A student, wishing to measure the chloride ion concentration in a number of water samples, constructed a galvanic cell using the AgCl electrode as one half-cell and a copper wire dipping into 1.00 M $CuSO_4$ solution as the other half-cell. In one analysis, the potential of the cell was measured to be 0.0895 V with the copper half-cell serving as the cathode. What was the chloride ion concentration in the water? (Take $E^\circ_{Cu^{2+}} = +0.3419$ V.)

6. At 25°C, a galvanic cell was set up having the following half-reactions:

$$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s); \qquad E^\circ_{Fe^{2+}} = -0.447 \text{ V}$$

$$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s); \qquad E^\circ_{Cu^{2+}} = +0.3419 \text{ V}$$

The copper half-cell contained 100 mL of 1.00 M $CuSO_4$. The iron half-cell contained 50.0 mL of 0.100 M $FeSO_4$. To the iron half-cell was added 50.0 mL of 0.500 M NaOH solution. The mixture was stirred and the cell potential was measured to be 1.175 V. Calculate the value of K_{sp} for $Fe(OH)_2$.

7. Suppose a galvanic cell was constructed at 25°C using a Cu/Cu^{2+} half-cell (in which the molar concentration of Cu^{2+} was 1.00 M) and a hydrogen electrode having a partial pressure of H_2 equal to 1 atm. The hydrogen electrode dipped into a solution of unknown hydrogen ion concentration, and the two half-cells were connected by a salt bridge. The precise value of $E^\circ_{Cu^{2+}} = +0.3419$ V.

(a) Derive an equation for the pH of the solution with the unknown hydrogen ion concentration, expressed in terms of E_{cell} and E°_{cell}.

(b) If the pH of the solution were 5.15, what would be the observed potential of the cell?

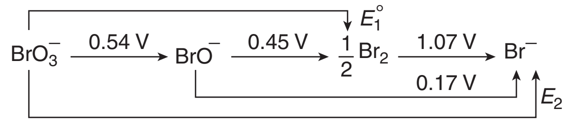
(c) If the potential of the cell were 0.645 V, what would be the pH of the solution?

8. How many grams of Cl_2 are produced when molten NaCl undergoes electrolysis at a current of 4.25 A for 35.0 min?

9. How many hours would it take to produce 75.0 g of metallic chromium by the electrolytic reduction of Cr^{3+} with a current of 2.25 A?

10. An unstirred solution of 2.00 M NaCl was electrolyzed for a period of 25.0 min and then titrated with 0.250 M HCl. The titration required 15.5 mL of the acid. What was the average current in amperes during the electrolysis?

11. From the standard potentials shown in the following diagram, calculate potentials E°_1 and E°_2.



12. Calculate the quantity of electricity that would be required to reduce 12.3 g of nitrobenzene to aniline if the current efficiency for the process is 50%. If the potential drop across the cell is 3 V, how much energy will be consumed?

13. An acidic solution of $CuSO_4$ containing 0.4 g of Cu^{2+} is electrolyzed until all the Cu is deposited. The electrolysis is continued for seven more minutes with the volume kept 100 mL and current 1.2 A. Calculate the volume of gases evolved at STP during entire electrolysis.

14. Calculate ΔG° and ΔS° (at 298 K) for the fuel cell reaction.

$$2H_2 + O_2 \rightarrow 2H_2O \text{ and}$$

$$E^\circ_{cell} = 1.23 \text{ V; and } \Delta H^\circ_{f(H_2O)} = -285.8 \text{ kJ mol}^{-1}$$

15. The standard reduction potential of Cu^{2+}/Cu is +0.34 V. Calculate the reduction potential at pH = 14 for the above couple in a saturated solution of cupric hydroxide. K_{sp} $(Cu(OH)_2) = 1 \times 10^{-19}$ M^3.

16. Calculate the standard cell potentials of galvanic cells in which the following reactions take place:

(a) $2Cr(s) + 3Cd^{2+}(aq) \rightarrow 2Cr^{3+}(aq) + 3Cd$

(b) $Fe^{2+}(aq) + Ag^{+}(aq) \rightarrow Fe^{3+}(aq) + Ag(s)$

Calculate the ΔG^o and equilibrium constant of the reactions.

17. In the button cells widely used in watches and other devices the following reaction takes place:

$$Zn(s) + Ag_2O(s) + H_2O(l) \rightarrow Zn^{2+}(aq) + 2Ag(s) + 2OH^-(aq)$$

Determine ΔG^o and E^o for the reaction.

18. For the cell reaction, $Sn(s) + Pb^{2+}(aq) \rightarrow Sn^{2+}(aq) + Pb(s)$ $E^o_{Sn^{2+}/Sn} = -0.136$ V, $E^o_{Pb^{2+}/Pb} = -0.126$ V. Calculate the ratio of concentration of Pb^{2+} to Sn^{2+} ion at which the cell reaction will be reversed?

19. The conductivity of sodium chloride at 298 K has been determined at different concentrations and the results are as follows:

Concentration (M)	0.001	0.010	0.020	0.050	0.100
$10^2 \times k$ (S m^{-1})	1.237	11.85	23.15	55.53	106.74

Calculate Λ_m for all concentrations and draw a plot between Λ_m and $C^{1/2}$. Find the value of Λ^0_m.

20. Three electrolytic cells A, B, C containing solutions of $ZnSO_4$, $AgNO_3$ and $CuSO_4$, respectively, are connected in series. A steady current of 1.5 A was passed through them until 1.45 g of silver deposited at the cathode of cell B. How long did the current flow? What mass of copper and zinc were deposited?

ADDITIONAL OBJECTIVE QUESTIONS

Single Correct Choice Type

1. The rusting of iron takes place as follows. Calculate $\Delta G°$ for the net process.

$$2H^+ + 2e^- + \tfrac{1}{2}O_2 \rightarrow H_2O(l); \quad E^o = +1.23\ \text{V}$$
$$Fe^{2+} + 2e^- \rightarrow Fe(s); \quad E^o = -0.44\ \text{V}$$

(A) –322 kJ mol^{-1} (B) –161 kJ mol^{-1}
(C) –152 kJ mol^{-1} (D) –76 kJ mol^{-1}

2. Specific conductance of 0.01 M KCl solution is x S cm^{-1}. When conductivity cell is filled with 0.01 M KCl the conductance observed is y S. When the same cell is filled with 0.01 M H_2SO_4, the observed conductance was z S cm^{-1}. Hence specific conductance of 0.01 M H_2SO_4 is:

(A) xz (B) z/xy
(C) xz/y (D) xy/z

3. When a sample of copper with zinc impurity is to be purified by electrolysis, the appropriate electrodes are:

Cathode	Anode
(A) Pure zinc	Pure copper
(B) Impure sample	Pure copper
(C) Impure zinc	Impure sample
(D) Pure copper	Impure sample

4. A current of 0.193 A is passed through 100 mL of 0.2 M NaCl for an hour. Calculate pOH of solution after electrolysis if current efficiency is 90%. Assume no volume change.

(A) 11.9 (B) 12.82
(C) 12.0 (D) 11.5

5. Find the equilibrium constant for the reaction, $2Fe^{3+} + 3I^- \rightleftharpoons 2Fe^{2+} + I^{3-}$. The standard reduction potentials in acidic conditions are 0.77 V and 0.54 V, respectively, for $Fe^{3+} | Fe^{2+}$ and $I^{3-} | I^-$ couples.

(A) 5.2×10^8 (B) 6.26×10^7
(C) 3.8×10^7 (D) 4.3×10^7

6. One coulomb of charge passes through solution of $AgNO_3$ and $CuSO_4$ connected in series and the conc. of two solutions being in the ratio 1:2. The ratio of weight of Ag and Cu deposited on Pt electrode is

(A) 107.9:63.54 (B) 54:31.77
(C) 107.9:31.77 (D) 54:63.54

7. When a lead storage battery is discharged,

(A) SO_2 is evolved.
(B) lead sulphate is consumed.
(C) lead is formed.
(D) H_2SO_4 is consumed.

8. Which of the following statements is true for the electrochemical Daniell cell ?

(A) Electrons flow from copper electrode to zinc electrode.
(B) Current flows from zinc electrode to copper electrode.
(C) Cations move towards copper electrode.
(D) Cations move towards zinc electrode.

9. The density of Cu in 8.94 g cm^{-3}. The quantity of electricity needed to plate an area 10 cm × 10 cm to a thickness of 10^{-2} using $CuSO_4$ solution would be

(A) 13586 C (B) 27172 C
(C) 40758 C (D) 20348 C

10. The specific conductance of a N/10 KCl solution at 18°C is 1.12×10^{-2} S cm^{-1}. The resistance of the solution contained in the cell is found to be 65 Ω. Calculate the cell constant.

(A) 0.912 cm^{-1} (B) 0.512 cm^{-1}
(C) 0.728 cm^{-1} (D) 0.632 cm^{-1}

11. The standard EMF of the cell in which the reaction

$$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

occurs is 0.59 V at 25°C. The equilibrium constant for the given reaction is approximately.

(A) 50
(B) 10
(C) 10^{50}
(D) 10^5

12. The specific conductance of a saturated AgCl solution is found to be 1.86×10^{-6} S cm^{-1} and that for water is 6.0×10^{-8} S cm^{-1}. The solubility of AgCl is (Λ^0_{eq} = 137.2 S $equiv.^{-1}$ cm^2)

(A) 1.7×10^{-3} mol L^{-1}
(B) 1.3×10^{-5} mol L^{-1}
(C) 1.3×10^{-4} mol L^{-1}
(D) 1.3×10^{-6} mol L^{-1}

13. In the electrolytic cell, flow of electrons is from

(A) cathode to anode through internal supply.
(B) cathode to anode through external supply.
(C) anode to cathode through internal supply.
(D) cathode to anode in solution.

14. A dilute aqueous solution of Na_2SO_4 is electrolyzed using platinum electrodes. The products at the cathode and anode are, respectively,

(A) H_2, O_2
(B) O_2, H_2
(C) O_2, Na
(D) O_2, SO_2

15. Faraday's laws of electrolysis are related to the

(A) atomic number of cation.
(B) atomic number of anion.
(C) equivalent weight of electrolyte.
(D) speed of the cation.

16. The useful work done during the reaction $Ag(s) + \frac{1}{2}Cl_2(g) \rightarrow AgCl(s)$ would be

(A) 110 kJ mol^{-1}
(B) 220 kJ mol^{-1}
(C) 55kJ mol^{-1}
(D) 100 kJ mol^{-1}

Given that: $E^{o}_{Cl_2/Cl^-} = 1.36\,V, E^{o}_{AgCl/Ag/Cl^-} = 0.220V, p_{Cl_2} = 1$ atm and T = 298K

17. The compound exhibiting maximum value of equivalent conductance in a fused state is

(A) $SrCl_2$
(B) $CaCl_2$
(C) $MgCl_2$
(D) $BeCl_2$

18. EMF of the cell $Ni|Ni^{2+}(0.1\,M)\,||\,Au^{3+}(1.0\,M)\,|\,Au$ will be (Given $E^{o}_{Ni/Ni^{2+}} = 0.25$ V, $E^{o}_{Au/Au^{3+}} = 1.5$ V)

(A) 1.75 V
(B) +1.7795 V
(C) +0.7795 V
(D) –1.7795 V

19. An alloy of Pb–Ag weighing 1.08 g was dissolved in dilute HNO_3 and the volume made to 100 mL. A silver electrode was dipped in the solution and the emf of the cell set-up as $Pt(s), H_2(g)|\,H^+(1M)||\,Ag^+(aq)|Ag(s)$ was 0.62 V. If E^{o}_{cell} is 0.80 V, what is the percentage of Ag in the alloy?
(At 25°C, $RT/F = 0.06$)

(A) 25
(B) 2.50
(C) 10
(D) 50

20. The EMF of the cell $M|M^{n+}(0.02\,M)||H^+(1\,M)|H_2(g)$ (1 atm), Pt at 25°C is 0.81 V. The valency of the metal if the standard oxidation potential of the metal is 0.76 V?

(A) 5
(B) 2
(C) 4
(D) 3

21. An electrochemical cell stops working after some time because

(A) one of the electrodes is eaten away.
(B) electode potentials of both the electrodes become equal in magnitude.
(C) electrode potentials of both electrodes go on decreasing.
(D) electode potentials of both the electrodes go on increasing.

22. Conductivity (units Siemens, S) is directly proportional to the area of the vessel and the concentration of the solution in it and is inversely proportional to the length of the vessel, then the unit of constant of proportionality is

(A) S m mol^{-1}
(B) S m^2 mol^{-1}
(C) S^{-2} m^2 mol
(D) S^2m^2 mol^{-2}

23. If the standard half-cell reduction potentials are 0.522 V for Cu^+/Cu and 0.3402 V for Cu^{2+}/Cu. The standard half-cell reduction potential for Cu^+/Cu^{2+} is

(A) 0.20 V
(B) 0.158 V
(C) 0.40 V
(D) 0.80 V

24. A solution containing one mole per liter of each $Cu(NO_3)_2$; $AgNO_3$; $Hg_2(NO_3)_2$; $Mg(NO_3)_2$ is being electrolyzed using inert electrodes. The values of standard electrode potentials (reduction potentials in volts are Ag/Ag^+ = 0.80 V, Hg/Hg_2^{2+} = 0.79 V, Cu/Cu^{2+} = –0.34 V, Mg/Mg^{2+} = +2.37 V. With increasing voltage, the sequence of deposition of metals on the cathode will be

(A) Ag, Hg, Cu
(B) Cu, Hg, Ag
(C) Ag, Hg, Cu, Mg
(D) Mg, Cu, Hg, Ag

25. In passing 3 F of electricity through the three electrolytic cells connected in series containing Ag^+, Ca^{2+} and Al^{+3} ions, respectively. The molar ratio in which the three metal ions are liberated at the electrodes is

(A) 1:2:3
(B) 3:2:1
(C) 6:3:2
(D) 3:4:2

26. The standard potentials at 25°C for the following half-cell reactions are given as

$$Zn^{+2} + 2e^- \rightarrow Zn; \quad E^{o}_{cell} = -0.762\ V$$

$$Mg^{2+} + 2e^- \rightarrow Mg; \quad E^{o}_{cell} = -2.37\ V$$

When zinc dust is added to a solution of magnesium chloride,

(A) no reaction will take place.
(B) zinc chloride is formed.
(C) zinc dissolve in solution.
(D) magnesium is precipitated.

27. Four alkali metals A, B, C and D have standard electrode potentials respectively as –3.05, –1.66, –0.40 and 0.80 V. Which one will be the most reducing?

(A) A
(B) B
(C) C
(D) D

28. $Zn(s) + Cl_2$ (1 atm) $\rightarrow Zn^{2+} + 2Cl^-$. The E^o of the cell is 2.12 V. To increase E,

(A) Zn^{2+} concentration should he increased.
(B) Zn^{2+} concentration should be decreased.
(C) Cl^- concentration should be increased.
(D) partial pressure Cl_2 should be decreased.

29. $Cr_2O_7^{2-} + I^- \rightarrow I_2 + Cr^{3+}$, $E^o_{cell} = 0.79$ V, $E^o_{Cr_2O_7^{2-}/Cr^{3+}} = 1.33$ V, $E^o_{I_2/I^-} = ?$
(A) 0.54 V (B) −0.054 V
(C) +0.18 V (D) −0.18 V

30. Value of $E^o_{H_2O/H_2\,(1\ atm)}$ at 298 K would be
(A) −0.207 V (B) +0.207 V
(C) −0.414 V (D) +0.414 V

31. Efficiency of the following cell is 84%

$$A(s) + B^{2+}(aq) \rightleftharpoons A^{2+}(aq) + B(s); \quad \Delta G^o = -285 \text{ kJ}$$

then the standard electrode potential of the cell will be
(A) 1.20 V (B) 2.40 V
(C) 1.10 V (D) 1.24 V

32. The standard emf of the cell
$Cd(s)|CdCl_2(0.1M)||AgCl(s)|\ Ag(s)$
in which the cell reaction is $Cd(s) + 2\,AgCl(s) \rightarrow 2Ag(s) + Cd^{2+}(aq) + 2Cl^-(aq)$ is 0.6915 V at 0°C and 0.6753 V at 25°C.
(A) −176 kJ (B) −334.7 kJ
(C) +123.5 kJ (D) −167 kJ

33. Calculate the emf of the cell
Pt, H_2 (1.0 atm)|CH_3COOH (0.1 M)||NH_3 (aq, 0.01 M)|H_2 (1.0 atm), Pt
Given that $K_a\,(CH_3COOH) = 1.8 \times 10^{-5}$, $K_b\,(NH_3) = 1.8 \times 10^{-5}$
(A) −0.92 V (B) −0.46 V
(C) −0.35 V (D) −0.20 V

34. An aqueous solution containing Na^+, Sn^{2+}, Cl^- and SO_4^{2-} ions, all at unit concentration, is electrolyzed between a silver anode and a platinum cathode. What changes occur at the electrodes when current passed through the cell? Given that $E^o_{Ag^+/Ag} = 0.799$ V $E^o_{Sn^{2+}/Sn} = -0.14$ V, $E^o_{Cl_2/Cl^-} = 1.36$ V, $E^o_{S_2O_8^{2-}/SO_4^{2-}} = 0.13$ V.
(A) Si^{2+} is reduced and Cl^- is oxidized.
(B) Ag is oxidized and Sn^{2+} is reduced.
(C) Sa^{2+} is reduced and Sn^{2+} is oxidized.
(D) H^+ is reduced and Sn^{2+} is oxidized.

35. Dal lake has water 8.2×10^{12} L, approximately. A power reactor produces electricity at the rate 1.5×10^6 C s^{-1} at an appropriate voltage. How many years would it take to electrolyze the lake?
(A) 2.4 million years (B) 5.3 million years
(C) 1.8 million years (D) 4.6 million years

36. In lead storage battery, during discharging process
(A) PbO_2 gets oxidized.
(B) H_2SO_4 is produced.
(C) density of H_2SO_4 solution decreases.
(D) density of H_2SO_4 solution increases.

37. The conductivity of a saturated solution of $BaSO_4$ is 3.06×10^{-6} S cm^{-1} and its equivalent conductance is 1.53 S cm^2 $equiv.^{-1}$. The K_{sp} for $BaSO_4$ will be
(A) 4×10^{-12} (B) 2.5×10^{-9}
(C) 2.5×10^{-13} (D) 4×10^{-6}

38. The EMF of the standard Weston cadmium cell Cd (12.5%) in Hg|$3CdSO_4 \cdot 8H_2O(s)$|std. sol. of $CdSO_4(l)$ $Hg_2SO_4(s)$|Hg is 1.0180 V at 25°C and the temperature coefficient of the cell EMF, $\left(\frac{\partial E}{\partial T}\right)_p = -4.0 \times 10^{-5}$ V deg^{-1}. Calculate ΔG, ΔH and ΔS for the reaction in the cell when $n = 2$.
(A) $\Delta G = -196.5$ kJ, $\Delta H = 198.8$ kJ, $\Delta S = -7.72$ J deg^{-1}
(B) $\Delta G = 196.5$ kJ, $\Delta H = 198.8$ kJ, $\Delta S = -7.72$ J deg^{-1}
(C) $\Delta G = 196.5$ kJ, $\Delta H = -198.8$ kJ, $\Delta S = -7.72$ J deg^{-1}
(D) $\Delta G = -196.5$ kJ, $\Delta H = 198.8$ kJ, $\Delta S = 7.72$ J deg^{-1}

39. If the molar conductance values of Ca^{2+} and Cl^- at infinite dilution are, respectively, 118.88×10^{-4} and 77.33×10^{-4} S m^2 mol^{-1}, then that of $CaCl_2$ is (S mm^2 mol^{-1}).
(A) 118.88×10^{-4} (B) 154.66×10^{-4}
(C) 273×10^{-4} (D) 196.21×10^{-4}

40. Best way to prevent rusting of iron is by
(A) making iron cathode. (B) putting it in saline water.
(C) both A and B. (D) none of these.

41. A current of 9.65 A is drawn from a Daniell cell for exactly 1 h. The loss in mass at anode and gain in mass at cathode, respectively, are
(A) 11.43 g, 11.77 g (B) 11.77 g, 11.43 g
(C) 22.86 g, 23.54 g (D) 23.54, 22.86 g

42. Consider the standard reduction potentials (in volts) as shown below. Find E^o.

$$\begin{tikzcd} SO_4^{2-} \arrow[r, "-0.936"] \arrow[rr, bend right, "E^o = ?"'] & SO_3^{2-} \arrow[r, "-0.576"] & \frac{1}{2}S_2O_3^{2-} \end{tikzcd}$$

(A) 0.326 V (B) 0.425 V
(C) 0.756 V (D) 0.512 V

43. The correct order of equivalent conductance at infinite dilution of (I) LiCl, (II) NaCl and (III) KCl
(A) I > II > III (B) III > II > I
(C) II > III > I (D) I > III > II

44. How much will potential of a hydrogen electrode change when its solution initially at pH = 0 is neutralized to pH = 7?
(A) It will increase by 0.0591 V.
(B) It will decrease by 0.0591 V.
(C) It will increase by 0.413 V.
(D) It will decrease by 0.413 V.

45. In an electrolysis of acidulated water, 4.48 L of hydrogen was produced by passing a current of 2.14 A. For how many hours was the current passed?
(A) 4 (B) 3
(C) 6 (D) 5

46. Construct the cell corresponding to the reaction: $3Cr^{2+}\,(1\ M) \rightarrow 2Cr^{3+}\,(1\ M) + Cr(s)$ and predict if the reaction is spontaneous. Also calculate the following ΔH and ΔS of the reaction at 25°C.

Given $E^{o}_{Cr^{3+},Cr} = 0.5$ V, $E^{o}_{Cr^{3+},Cr^{2+}} = -0.41$ V and ΔG of the reaction at 35°C = –270.50 kJ

(A) $\Delta H = -51.05$ kJ, $\Delta S = 700$ kJ K^{-1}
(B) $\Delta H = -31.05$ kJ, $\Delta S = -700$ kJ K^{-1}
(C) $\Delta H = -51.05$ kJ, $\Delta S = 706$ kJ K^{-1}
(D) $\Delta H = -53.05$ kJ, $\Delta S = 706$ kJ K^{-1}

47. Electrolysis of a solution of HSO_4^- ions produces $S_2O_8^{2-}$. Assuming 75% current efficiency, what current should be employed to achieve a production rate of 1 mol S_2O_8 per hour?

(A) 43.3 A (B) 71.5 A
(C) 35.2 A (D) 58.3 A

48. By how much would the oxidizing power of the $(MnO_4^-|Mn^{2+})$ couple change if the H^+ ions concentration is decreased 100 times at 25°C?

(A) It will increase by 189 mV.
(B) It will decrease by 189 mV.
(C) It will increase by 19 mV.
(D) It will decrease by 19 mV.

49. How many grams of silver could be plated out on a serving tray by electrolysis of a solution containing Ag(I) for a period of 8.0 h at a current of 8.46 A? What is the area of the tray if the thickness of the silver plating is 0.00254 cm? (Density of silver is 10.5 g cm^{-3}.)

(A) 124.18 g, 1.02×10^{-5} cm^2
(B) 124.18 g, 1.02×10^{-2} cm^2
(C) 272.18 g, 1.02×10^{-4} cm^2
(D) 272.18 g, 1.02×10^{-2} cm^2

50. For HCl solution at 25°C, the equivalent conductivity at infinite dilution is 425 S cm^{-1}equiv.$^{-1}$. The specific conductance of a solution of HCl is 3.825 S cm^{-1}. If the apparent degree of dissociation is 90%, the normality of solution is

(A) 0.9 N (B) 10.00 N
(C) 1.1 N (D) 1.2 N

51. The number of coulombs required to reduce 12.3 g of nitrobenzene to aniline is

(A) 96,500 C (B) 5790 C
(C) 95,700 C (D) 57,900 C

52. Molar conductances of $BaCl_2$, H_2SO_4 and HCl at infinite dilutions are x_1, x_2 and x_3, respectively, equivalent conductance of $BaSO_4$ at infinite dilution will be

(A) $(x_1 + x_2 - x_3)/2$ (B) $x_1 + x_2 - 2x_3$
(C) $(x_1 - x_2 - x_3)/2$ (D) $(x_1 + x_2 - 2x_3)/2$

53. Which among the following has maximum potential for the half-cell reaction: $2H^+ + 2e^- \rightarrow H_2$?

(A) 1.0 M HCl (B) 1.0 M NaOH
(C) Pure water (D) A solution with pH = 4

54. If the hydrogen electrodes in two solutions of pH = 3 and pH = 6 are connected by a salt bridge, the emf of the resulting cell is

(A) 0.177 V (B) 0.3 V
(C) 0.052 V (D) 0.104 V

Multiple Correct Choice Type

1. Which of the following aqueous solution turn(s) alkaline after electrolysis?

(A) NaCl (B) $CuCl_2$
(C) CH_3COONa (D) K_2SO_4

2. For the cell $Tl|Tl^+(0.001\ M)\,||\,Cu^{2+}(0.1\ M)\,|\,Cu$. Given that E_{cell} is 0.83 V which can be increased

(A) by increasing $[Cu^{2+}]$. (B) by increasing $[Tl^+]$.
(C) by decreasing $[Cu^{2+}]$. (D) by decreasing $[Tl^+]$.

3. We observe blue color if

(A) Cu electrode is placed in the $AgNO_3$ solution.
(B) Cu electrode is placed in the $ZnSO_4$.
(C) Cu electrode is placed in the dil. HNO_3.
(D) Cu electrode is placed in the $NiSO_4$.

4. In which of the following $(E_{cell} - E^{o}_{cell}) = 0$

(A) $Zn|Zn^{2+}$ (0.01 M)$||Ag^+$ (0.1 M) | AgO(s)
(B) $Pt|H_2$(1 atm)|pH = 1$||Zn^{2+}$(0.01 M)|Zn
(C) $Pt|H_2$(1 atm)|pH = 1$||Zn^{2+}$(1 M)|Zn
(D) $Pt|H_2$(1 atm)$|H^+$(0.01 M)$||Zn^{2+}$(0.01 M)|Zn

5. Process inside the cell is exothermic when

(A) $\left[\frac{\partial E}{\partial T}\right] < 0$ (B) $\left[\frac{\partial E}{\partial T}\right] = 0$
(C) $\Delta H > nFE$ (D) $\Delta H = nFE$

6. Equal quantity of electricity is passed through three electrolytic cells containing aqueous solutions of $FeSO_4$, $Fe_2(SO_4)_3$ and $Fe(NO_3)_3$. Regarding the electrolytic process which of the following is/are correct, assuming at cathode only iron is reduced.

(A) The amount of iron deposited in the three cases is equal.
(B) The amount of iron deposited in $Fe_2(SO_4)_3$ and $Fe(NO_3)_3$ is equal.
(C) Same gas is evolved at anode in all three electrolytic processes.
(D) Amount of iron deposited in $Fe_2(SO_4)_3$ is double to that of the iron deposited in case of $Fe(NO_3)_3$.

7. Which of the following statements is (are) correct?

(A) The reactivity of metals decreases in going down the electrochemical series.
(B) A metal can displace any other metal placed above it in the electrochemical series from its salt solution.
(C) The oxidizing power of the substances decrease from the top to the bottom in the electrochemical series.
(D) A redox reaction is feasible when the substance having higher reduction potential gets reduced and the one having lower reduction potential gets oxidized.

8. Hydrogen gas will reduce

(A) heated cupric oxide.
(B) heated silver oxide.
(C) heated zinc oxide.
(D) heated aluminium oxide.

9. Which of the following statements is (are) not correct?
(A) Metallic conduction is due to the movement of electrons whereas the electrolytic conduction is due to the movement of ions.
(B) Both metallic and electrolytic conduct ions involve transfer of matter.
(C) Electrolytic conduction decreases with rise in temperature.
(D) Metallic conduction involves no chemical change.

10. Select the correct statements if 9.65 A current is passed for 1 h through the cell $\text{Ag}\,|\,\text{Ag}^+(1\text{ M})\,||\,\text{Cu}^{2+}(1\text{ M})\,|\,\text{Cu}$
(A) Ag will oxidize to Ag^+ and new $[Ag^+] = 1.36$ M
(B) Ag^+ will reduce to Ag and new $[Ag^+] = 0.64$ M
(C) Cu^{2+} will reduce to Cu and new $[Cu^{2+}] = 0.82$ M
(D) Cu will oxidize to Cu^{2+} and new $[Cu^{2+}] = 0.82$ M

11. The tarnishing of silver ornaments in atmosphere is due to the formation of
(A) Ag_2O
(B) Ag_2S
(C) Ag_2CO_3
(D) Ag_2SO_4

12. Which of the following statements are correct?
(A) Ionic mobility is directly proportional to the velocity of the ion.
(B) Ionic mobility of an ion decreases if potential gradient increases.
(C) Conductance of an electrolyte solution decreases if the interionic forces of attraction are high.
(D) Conductance = $F \times$ Ionic mobility

13. In the electrolysis of which of the following aqueous solutions, pH remains constant (assuming no change in volume)
(A) K_2SO_4
(B) $AgNO_3$
(B) $CuCl_2$
(D) NaCl

14. The standard emf of the cell, Cd(s)|$CdCl_2$(aq)||AgCl(s)|Ag(s) in which the cell reaction is 0.6195 V at 0°C and 0.6753 V at 25°C. The value of ΔH of the reaction at 25°C is
(A) 167.26 kJ mol^{-1}
(B) –167.26 kJ mol^{-1}
(C) 40 kJ mol^{-1}
(D) –40 kJ mol^{-1}

15. Which are true for a standard hydrogen electrode?
(A) The hydrogen ion concentration is 1 M.
(B) Temperature is 25°C.
(C) Pressure of hydrogen is 1 atm.
(D) It contains a metallic conductor which does not adsorb hydrogen.

16. In which of the following electrolytes, KCl cannot be used in salt bridge?
(A) Solution of silver
(B) Solution of mercurous ion
(C) Solution of thallous salt
(D) Solution of Zn^{2+} ions

17. Which of the following are concentration cells?
(A) $\text{Pt, H}_2(\text{g})(p_1)\,|\,\text{HCl}\,|\,\text{H}_2(\text{g})(p_2),\text{Pt}$
(B) $\text{Cd(Hg)}(a_1)\,|\,\text{Cd}^{2+}(C)\,|\,\text{(Hg)Cd}\,(a_2)$
(C) $\text{Zn(s)}\,|\,\text{Zn}^{2+}(C_1)\,||\,\text{Cu}^{2+}(C_2)\,|\,\text{Cu}$
(D) $\text{Ag}\,|\,\text{AgCl}\,|\,\text{Cl}^-(\text{aq})\,(C_1)\,||\,\text{Br}^-(\text{aq})\,(C_2)\,|\,\text{AgBr}\,|\,\text{Ag}$

18. When a nickel spatula is used to stir an aqueous copper sulphate solution,
(A) the solution is stirred well without any chemical change.
(B) nickel spatula gets partly oxidized into Ni^{2+} ions.
(C) Cu^{2+} ions present in the solution get partly reduced into Cu.
(D) copper gets deposited on the spatula.

19. Select the wrong relations.

(A) $\Delta S = \left(\dfrac{\partial E}{\partial T}\right)_p \times nF$
(B) $-\Delta S = \left(\dfrac{\partial E}{\partial T}\right)_p \times nF$
(C) $\left(\dfrac{\partial E}{\partial T}\right)_p = \left(\dfrac{\partial \Delta S}{\partial T}\right)$
(D) $\left(\dfrac{\partial E}{\partial T}\right)_p = \dfrac{\Delta H + nEF}{T}$

20. Saturated solution of KNO_3 is used to make salt bridge because
(A) velocity of K^+ greater than that of NO_3^-.
(B) velocity of NO_3^- is greater than that of K^+.
(C) velocity of both K^+ and NO_3^- are nearly the same.
(D) K^+ has very low reduction potential and NO_3^- has very low oxidation potential.

21. In which of the following salt bridge is not needed?
(A) Pb|$PbSO_4$(s)|H_2SO_4(aq)|PbO_2(s)|Pb
(B) Cd|CdO(s)|KOH(aq)|NiO_2(s)|Ni
(C) Fe(s)|FeO(s)|KOH(aq)|Ni_2O_3(s)|Ni
(D) Zn|$ZnSO_4$|$CuSO_4$(aq)|Cu

Assertion–Reasoning Type

Choose the correct option from the following:
(A) Statement 1 and Statement 2 are True; Statement 2 is the correct explanation of the Statement 1.
(B) Statement 1 and Statement 2 are True; Statement 2 is NOT a correct explanation of the Statement 1.
(C) Statement 1 is True, Statement 2 is False.
(D) Statement 1 is False, Statement 2 is True.

1. **Statement 1:** If an aqueous solution of NaCl is electrolyzed, the product obtained at the cathode is H_2 gas and not Na.
Statement 2: Gases are liberated faster than the metals.

2. **Statement 1:** Specific conductance decreases with dilution ion, whereas equivalent conductance increases.
Statement 2: On dilution, the number of ions per milliliter decreases, but the total number of ions increases considerably.

3. **Statement 1:** On increasing dilution, the specific conductance keeps on increasing.
Statement 2: On increasing dilution, degree of ionization of weak electrolyte increases and mobility of ions also increases.

4. **Statement 1:** For the Daniell cell, Zn|Zn^{2+}||Cu^{2+}|Cu with $E_{\text{cell}} = 1.1$ V, the application of opposite potential greater than 1.1 V results into flow of electrons from cathode to anode.
Statement 2: Zn is deposited at anode and Cu is dissolved at cathode.

5. **Statement 1:** Zinc displaces copper from copper sulphate solution.
   Statement 2: Lesser number of ions are available per g equivalent at higher concentration.
6. **Statement 1:** Calomel electrode especially with saturated KCl solution is used as a reference electrode, that is, secondary standard electrode.
   Statement 2: The potential of calomel electrode depends upon the concentration of Cl^- ions.
7. **Statement 1:** Salt bridge maintains electrical neutrality in two half-cells.
   Statement 2: Salt bridge transfer ions from one solution to other.

Comprehension Type

Read the paragraphs and answer the questions that follow.

Paragraph I

Molar conductance of NaCl varies with concentration according to the equation $\Lambda_m = \Lambda_m^0 - b\sqrt{C}$ where Λ_m is molar specific conductance, Λ_m^0 is molar specific conductance at infinite dilution, and C is the molar concentration. The variation is shown in the following table:

Molar concentration of NaCl	Molar conductance in S cm^2 mol^{-1}
4×10^4	107
9×10^4	97
16×10^{-4}	87

1. When a certain conductivity cell (C) was filled with 25×10^{-4} (M) NaCl solution. The resistance of the cell was found to be 1000 ohms. At infinite dilution, conductance of Cl^- and SO_4^{2-} are 80 S cm^2 mol^{-1} and 160 S cm^2 mol^{-1}, respectively. What is the molar conductance of NaCl at infinite dilution?
   (A) 147 S cm^2 mol^{-1} (B) 107 S cm^2 mol^{-1}
   (C) 127 S cm^2 mol^{-1} (D) 157 S cm^2 mol^{-1}
2. What is the cell constant of the conductivity cell (C) ?
   (A) 0.385 cm^{-1} (B) 3.85 cm^{-1}
   (C) 38.5 cm^{-1} (D) 0.1925 cm^{-1}
3. If the cell (C) is filled with 5×10^{-3} (N) Na_2SO_4, the observed resistance was 400 ohm. What is the molar conductance of Na_2SO_4?
   (A) 19.25 S cm^2 mol^{-1} (B) 96.25 S cm^2 mol^{-1}
   (C) 385 S cm^2 mol^{-1} (D) 192.5 S cm^2 mol^{-1}

Paragraph II

Pb is used at anode and PbO_2 at cathode in a lead storage battery, while concentrated H_2SO_4 is used as electrolyte. The battery holds 3.5 L acid with it. During the discharge process, the density of acid falls from 1.294 to 1.139 g mL^{-1}. Given that the sulphuric acid of density 1.294 g mL^{-1} is 39% by mass and that of density 1.139 g mL^{-1} is 20% by mass.

4. Equivalent mass of sulphuric acid in lead storage battery is
   (A) 49 (B) 98
   (C) 24.5 (D) none of these.
5. Normalities of sulphuric acid before and after discharge are
   (A) 5.15, 2.32 (B) 2.32, 5.15
   (C) 5.15, 5.15 (D) 2.32, 2.32
6. The number of ampere-hours for which the battery must have been used is
   (A) 26504 Ah (B) 2650.4 Ah
   (C) 265.04 Ah (D) 26.504 Ah
7. The amount of charge which the battery must have been used is
   (A) 9.88 F (B) 8.98 F
   (C) 8.89 F (D) 7.88 F
8. Which of the following takes place in discharge process at anode?
   (A) $PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$
   (B) $PbSO_4 + 2H_2O \rightarrow PbO_2 + 4H^+ + SO_4^{2-} + 2e^-$
   (C) $Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e^-$
   (D) $PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$

Paragraph III

At equilibrium, the driving force ΔG is equal to zero, just as in any other spontaneous process. Both ΔG and E_{cell} are zero when the redox reaction is at equilibrium. The Nernst equation for the redox process of the cell is:

$$E_{cell} = E^o_{cell} - \frac{0.059}{n}\log Q$$

where Q is the reaction quotient and the standard cell potential E^o is derived from the standard Gibbs energy change as

$$E_{cell} = -\frac{\Delta G^o}{nF}$$

At equilibrium, the Nernst equation is

$$E^o_{cell} = \frac{0.059}{n}\log K_C$$

9. On the basis of information available for the reaction
   $$\tfrac{4}{3}Al + O_2 \rightarrow \tfrac{2}{3}Al_2O_3;\quad \Delta G = -827\ \text{kJ mol}^{-1}\ \text{of}\ O_2$$
   the minimum emf required to carry out an electrolysis of Al_2O_3 is (Given 1 F = 96500 C)
   (A) 2.14V (B) 4.28V
   (C) 6.42 V (D) 8.56 V
10. The nature of graph of E^o_{cell} against log K_C is a/an
    (A) straight line. (B) parabola.
    (C) hyperbola. (D) elliptical curve.
11. The equilibrium constant K_C for the reaction $Cu(s) + 2Ag^+(aq) \rightleftharpoons Cu^{2+}(aq) + 2Ag(s)$ $(E^o_{cell} = 0.46\ V)$ will be
    (A) antilog 15.6 (B) antilog 2.5
    (C) antilog 1.5 (D) antilog 12.2

Integer Answer Type

The answer is a **non-negative integer**.

1. For the Mg–Ag cell, if concentration of Mg^{2+} ions is changed from 0.1 M to 0.01 M and that of Ag^+ ions is changed from 0.5 M to 0.25 M, the number of times the difference between the emf of the cell and its standard emf will change is ________.

2. Calculate the volume of Cl_2 at NTP produced during electrolysis of $MgCl_2$ which produces 6.50 g Mg. (atomic weight of Mg = 24.3 u).

3. When water is electrolyzed, hydrogen and oxygen gases are produced. If 1.008 g of H_2 is liberated at cathode, the mass of O_2 formed at the anode is ________.

4. At equimolar concentration of Fe^{2+} and Fe^{3+} what must $[Ag^+]$ be so that the voltage of the galvanic cell made from Ag^+/Ag and Fe^{3+}/Fe^{2+} electrodes equals zero? The reaction is $Fe^{2+} + Ag^+ \rightleftharpoons Fe^{3+} + Ag$. Determine the equilibrium constant at 25°C for the reaction. Given: $E^o_{Ag^+/Ag} = 7.99$ V and $E^o_{Fe^+/Fe^{2+}} = 0.771$ V.

5. Cd amalgam is prepared by electrolysis of a solution of $CdCl_2$ using a mercury cathode. Find how long should a current of 5 A be passed in order to prepare 12% Cd-Hg amalgam on a cathode of 2.56 g mercury? (Atomic weight of Cd = 112.40 u).

6. The equilibrium constant for the following reaction at 298 K is expressed as $x \times 10^y$.

$$2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2, E^o_{cell} = 0.235 \text{ V}.$$

The value of y is ________.

7. The standard oxidation potential of Ni/Ni^{2+} electrode is 0.236 V. If this is combined with a hydrogen electrode in acid solution, at what pH of the solution will the measured emf be zero at 25°C? (Assume $[Ni^{2+}]$ = 1 M and $p_{H_2} = 1$ atm)

Matrix–Match Type

1. Match the cell with its applications

Column I	Column II
(A) Nickel–Cadmium cell	(p) Used in auto vehicles
(B) Lithium battery	(q) Secondary cell
(C) H_2–O_2 cell	(r) Fuel cell
(D) Lead storage battery	(s) Used in Apollo spacecraft

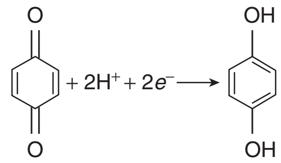
2. Match the cell with its characteristics

Column I	Column II
(A) Concentration cell	(p) Fe is oxidized by Ni_2O_3
(B) Edison cell	(q) Zinc anode
(C) Mercury cell	(r) Hg cathode
(D) Dry cell	(s) $E^o = 0$

3. For the galvanic cell $Ag|Ag^+_{(eq)}(0.1M)||Cd^{2+}_{(aq)}(0.1M)Cd$, $E^o_{Ag^+/Ag} = 0.80$ V, $E^o_{Cd^{2+}/Cd} = -0.40$ V. Match the quantities with their values.

Column I	Column II
(A) The cell reaction	(p) –1.17 V
(B) Reaction quotient	(q) –1.20 V
(C) The cell potential	(r) Non-spontaneous
(D) The standard cell potential	(s) 1/10
	(t) $E^o_{cell} = E^o_{cathode} - E^o_{anode}$

4. Match the electrode with its composition.

Column I	Column II
(A) Concentration cell	(p) 
(B) Electrode reversible with respect to anion	(q) $Pt|Hg_2Cl_2$, KCl
(C) Quinhydrone electrode	(r) Na(Hg) | NaCl | Na (Hg)
(D) Redox electrode	(s) Ag/AgCl, Cl^-

ANSWERS

Review Questions

1. If E^o for copper is taken to be 0 V, then E^o for hydrogen must be 0.34 V.

4. 0.10 mol of Cr from a Cr^{3+} solution

7. Copper will deposit a greater mass of metal

9. The hydrogen is held in a metal alloy, Mg_2Ni. The electrolyte is KOH

13. $Br_2(aq) + 2I^-(aq) \rightarrow I_2(s) + 2Br^-(aq)$

14. **(a)** $Fe(s)|Fe^{2+}(aq)||Cd^{2+}(aq)|Cd(s)$; **(b)** $Ag(s)|Ag^+(aq)||Ni^{2+}(aq),H^+(aq)|NiO_2(s)|Pt(s)$; **(c)** $Mg(s)|Mg^{2+}(aq)||Cd^{2+}(aq)|Cd(s)$

15. $BrO_3^-(aq) + 6I^-(aq) + 6H^+(aq) \rightarrow 3I_2(s) + Br^-(aq) + 3H_2O$; $E^o_{cell} = 0.90$ V.

16. $4HOCl(aq) + 2H^+(aq) + S_2O_3^{2-}(aq) \rightarrow 2Cl_2(g) + H_2O + 2H_2SO_3(aq)$

17. **(a)** Nickel will reduce copper. **(b)** Blue color of the solution fades due to reduction of Cu^{2+} ions to Cu.

18. $Ag^+/Ag < Cu^{2+}/Cu < Fe^{2+}/Fe < Cr^{3+}/Cr < Mg^{2+}/Mg < K^+/K$

21. **(a)** As $E^\circ = 0$ for concentration cell and $C_1/C_2 = 0.001$, so $E_1/E_2 = 2$. **(b)** As $E^\circ = 0$ for concentration cell and $C_1 = C_2$, therefore, $E_{\text{cell}} = 0$. So, there is no electricity in the cell.

22. **(a)** Decreases; **(b)** increases; **(c)** does not vary much

24. Overall change in pH is 0. K_2SO_4 serves as charge carriers to balance the charge that occurs upon electrolysis of the K_2SO_4 solution.

25. In solid NaCl, the ions are held in place and cannot move about.

Numerical Problems

1. 1.0×10^2 kJ

2. -1.63×10^3 kJ

3. 0.31

4. 0.155 V

5. 0.310 M

6. 1.96×10^{-15}

7. **(a)** $\dfrac{(E_{\text{cell}} - E^\circ_{\text{cell}})}{0.0592} = -\log[\text{H}^+] = \text{pH}$; **(b)** 0.647 V; **(c)** 5.12

8. 3.28 g

9. 51.5 h

10. 0.250 A

11. $E_1^\circ = 0.52$ V and $E_2^\circ = 0.61$ V

12. –1158900 C, 28.9 kJ

13. 158.14 mL ($H_2 + O_2$)

14. $\Delta G^\circ = -474.78$ kJ, $\Delta S^\circ = +634.16$ J K^{-1}

15. –0.22 V

16. **(a)** 3.192×10^{34}; **(b)** 3.22

20. 863 s, 0.426 g Cu, 0.438 g Zn

Additional Objective Questions

Single Correct Choice Type

1. (A)
2. (C)
3. (D)
4. (B)
5. (B)
6. (C)
7. (D)
8. (C)
9. (B)
10. (A)
11. (C)
12. (B)
13. (B)
14. (A)
15. (C)
16. (A)
17. (A)
18. (B)
19. (C)
20. (B)
21. (B)
22. (B)
23. (B)
24. (A)
25. (C)
26. (A)
27. (A)
28. (B)
29. (A)
30. (C)
31. (D)
32. (D)
33. (B)
34. (C)
35. (C)
36. (C)
37. (D)
38. (A)
39. (B)
40. (A)
41. (B)
42. (C)
43. (B)
44. (D)
45. (D)
46. (D)
47. (B)
48. (B)
49. (C)
50. (B)
51. (D)
52. (B)
53. (A)
54. (B)

Multiple Correct Choice Type

1. (A, B, C, D)
2. (A, D)
3. (A, C)
4. (A, B, C, D)
5. (A, B, C, D)
6. (B, C)
7. (A, D)
8. (A, B)
9. (A, B)
10. (A, C)
11. (A, B)
12. (A, B, D)
13. (A, B)
14. (B, D)
15. (A, B, C)
16. (A, D)
17. (A, B, D)
18. (B, C, D)
19. (A, D)
20. (A, C, D)
21. (A, B, C)

Assertion–Reasoning Type

1. (C)
2. (A)
3. (D)
4. (B)
5. (A)
6. (B)
7. (C)

Comprehension Type

1. (C)
2. (D)
3. (D)
4. (B)
5. (A)
6. (C)
7. (A)
8. (B)
9. (A)
10. (A)
11. (A)

Integer Answer Type

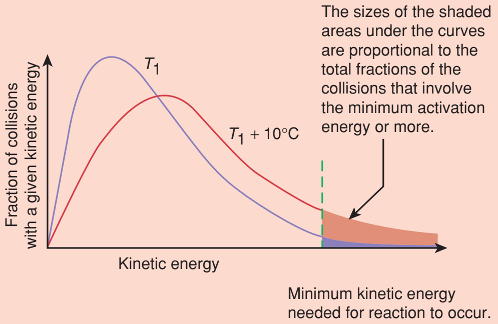
1. (2)
2. (6)
3. (8)
4. (3)
5. (2)
6. (7)
7. (4)

Matrix–Match Type

1. A → (q); B → (q); C → (r, s); D → (p, q)
2. A → (s); B → (p); C → (q, r); D → (q)
3. A → (q, r); B → (s); C → (p, t); D → (q)
4. A → (r); B → (q); C → (p); D → (s)

12

Chemical Kinetics



Kinetic energy distributions for a reaction mixture at two different temperatures

Contents

12.1 Rate of a Chemical Reaction
12.2 Factors Influencing Rate of a Reaction
12.3 Differential Rate Expression and Rate Constant
12.4 Elementary and Complex Reactions
12.5 Molecularity of a Reaction
12.6 Order of a Reaction
12.7 Calculations of Order and Molecularity Based on Reaction Mechanisms
12.8 Pseudo Order Reactions
12.9 Integrated Rate Equations
12.10 Half-Life of Reactions and Radioactivity
12.11 Derivation of Rate Laws for Complex Reactions Using Integrated Rate Equations
12.12 Determination of Order of Simple Reactions – Experimental Methods
12.13 Effect of Temperature – Arrhenius Theory
12.14 Effect of Catalyst
12.15 Collision Theory

Chemical reactions take place at different speeds. Some, such as the rusting of iron or the breakdown of plastics in the environment, take place very slowly. Others, like the combustion of petrol or the explosion of gunpowder, occur very quickly. Some reactions take place instantaneously, like a freshly exposed surface of metallic sodium tarnishes almost instantly when exposed to air and moisture. There are other reactions that proceed at moderate rate, like burning of a log of wood or hydrolysis of starch. Thermodynamics predicts if the chemical reaction will take place and the formation of product is spontaneous or not depending upon its thermodynamical stability. It does not, however predict in how much time the reaction would be complete. **Chemical kinetics** is the study of the speeds (or *rates*) of chemical reactions. On a practical level, it is concerned with factors that affect the speeds of reactions and how reaction speeds can be controlled.

To understand the path of the reactions, reactions should be moderately slow so that their intermediates can be isolated and characterized, and the mechanism of the reaction can be elucidated. Hence, *chemical kinetics deals with the study of the rate of chemical reactions and with the elucidation of the mechanisms by which they proceed*.

Consider the following reaction. Thermodynamics predicts that the reaction should form SO_3, not SO_2, because SO_3 is more stable than SO_2.

$$CS_2(g) + 3O_2(g) \rightarrow CO_2(g) + 2SO_2(g)$$

Under normal conditions, however, this reaction invariably stops at SO_2 because the reaction between SO_2 and O_2 to form SO_3 is extremely slow. Hence, to fully understand chemical reactions, we need to combine the predictions of thermodynamics with studies of the factors that influence the rates of chemical reactions.

12.1 | RATE OF A CHEMICAL REACTION

One of the first kinetic experiments was done in 1850 by Ludwig Wilhemy, a lecturer in physics at the University of Heidelberg. Wilhemy studied the rate at which sucrose, or cane sugar, reacts with acid to form a mixture of fructose and glucose known as invert sugar.

$$\text{Sucrose (aq)} + H_3O^+\text{(aq)} \rightarrow \underbrace{\text{Glucose (aq)} + \text{Fructose (aq)}}_{\text{Invert sugar}}$$

Wilhemy found that the rate at which sucrose is consumed in this reaction is directly proportional to the concentration of the sucrose in the solution when the pH and temperature of the solution are held constant. The rate of the reaction at any moment in time can, therefore, be described by the following equation, in which k is the proportionality constant and [sucrose] is the concentration of sucrose in units of moles per liter at that moment.

$$\text{Rate} = k[\text{Sucrose}]$$

Since the sucrose concentration decreases as sucrose is consumed in the reaction, the rate of the reaction gradually decreases with time.

The **rate** or **velocity** of a chemical reaction can be defined as the rate of appearance of one or more of its products, or as the rate of disappearance of one or more of its reactants in unit time. When chemical reactions occur, the concentrations of reactants decrease as they are used up, while the concentrations of the products increase as they form (Fig. 12.1).

Reaction's rate can be found by measuring the change in concentration per unit of time of one substance. The rate is the rate of the reaction *with respect to that substance.*

$$\text{Rate with respect to X} = \frac{(\text{Conc. of X at time } t_{\text{final}} - \text{Conc. of X at time } t_{\text{initial}})}{(t_{\text{final}} - t_{\text{initial}})}$$

$$= \frac{\Delta(\text{Conc. of X})}{\Delta t}$$

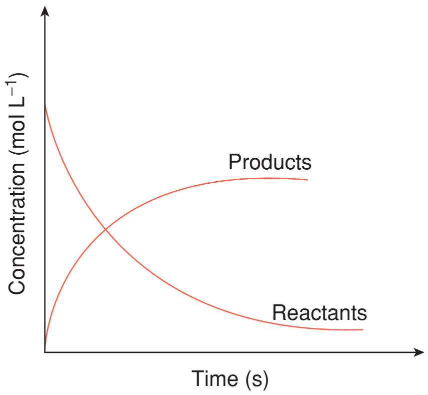


Figure 12.1 Variation of concentration with time.

Molarity (mol L^{-1}) is normally the concentration unit, and the second (s) is the most often used unit of time. Therefore, the units for reaction rates are most frequently the following mol L^{-1} s^{-1}. For instance, if the concentration of one product of a reaction increases by 0.50 mol L^{-1} each second, the rate of its formation is 0.50 mol L^{-1} s^{-1}. Similarly, if the concentration of a reactant decreases by 0.20 mol L^{-1} s^{-1}, its rate of reaction is 0.20 mol L^{-1} s^{-1}. By convention, **reaction rate is reported as a positive value whether something increases or decreases in concentration**. In case of gaseous reactions, the concentration is expressed in terms of partial pressure of gases and hence the rate is expressed in units of atm s^{-1}.

Average and Instantaneous Rates

Consider a reaction where one mole of reactant A is converted into product B.

$$A \rightarrow B$$

Let $[A]_1$ and $[A]_2$ be the concentration of the reactant at times t_1 and t_2 and $[B]_1$ and $[B]_2$ be the concentration of the product at t_1 and t_2, respectively. We use square brackets to signify concentrations specifically in moles per liter; [A] thus means the molar concentration of A. Then change in concentration of reactants and products between the time interval Δt $(= t_2 - t_1)$ is

$$\Delta A = [A]_2 - [A]_1$$
$$\Delta B = [B]_2 - [B]_1$$

The rate of reaction can be measured as rate of disappearance reactant A or rate of formation of component B. It can be expressed mathematically as

$$\text{Rate} = \frac{\text{Decrease in concentration of A}}{\text{Time interval}} = -\frac{\Delta A}{\Delta t} \quad (12.1)$$

or
$$\text{Rate} = \frac{\text{Increase in concentration of B}}{\text{Time interval}} = +\frac{\Delta \text{B}}{\Delta t} \tag{12.2}$$

Since the concentration of A decreases, the change in its concentration is negative. It is multiplied by −1 to obtain the rate of reaction which is always a positive quantity. The rate obtained from Eqs. (12.1) and (12.2) is called the **average rate of reaction** and is represented as r_{avg}. It depends on the time interval between which it is measured and the concentration of reactants and products.

A reaction rate is generally not constant throughout the reaction but commonly changes as the reactants are used up. This is because the rate usually depends on the concentrations of the reactants, and these change as the reaction proceeds.

The rate at which a reactant is being consumed at any particular moment is called the **instantaneous rate**. Mathematically, the instantaneous rate can be determined by measuring the average rate in the smallest time interval dt (i.e., as Δt approaches zero). Thus for the reaction A → B, the instantaneous rate can be expressed using average rate as

$$r_{\text{avg}} = \frac{-\Delta \text{A}}{\Delta t} = \frac{\Delta \text{B}}{\Delta t}$$

As $\Delta t \to 0$, $r_{\text{avg}} \to r_{\text{inst}}$ or

$$r_{\text{inst}} = \frac{-\text{dA}}{\text{d}t} = \frac{\text{dB}}{\text{d}t} \tag{12.3}$$

Graphically, the two rates may be represented as shown in Fig. 12.2.

Note: When we use the term "reaction rate" we mean instantaneous rate, unless stated otherwise.

For reactions in which the stoichiometric coefficients of the reactants and products are the same, as in decomposition of thionyl chloride (SO_2Cl_2), the rate of disappearance of any of the reactants is same as the rate of appearance of the products.

$$SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$$

The rate of reaction may be given as

$$\text{Rate of reaction} = -\frac{\Delta[SO_2Cl_2]}{\Delta t} = \frac{\Delta[SO_2]}{\Delta t} = \frac{\Delta[Cl_2]}{\Delta t}$$

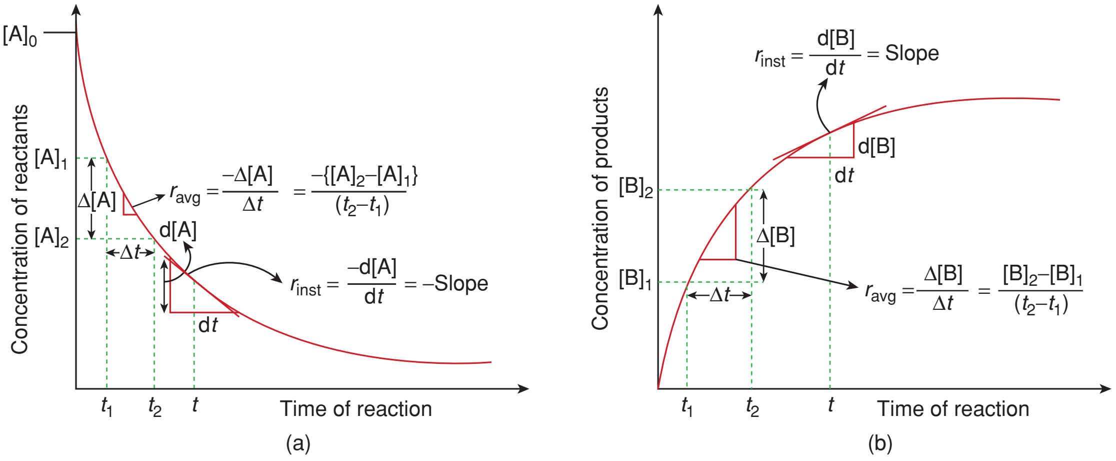


Figure 12.2 Representation of (a) instantaneous and (b) average rates.

For reactions in which the stoichiometric coefficients of the reactants and products are not the same, the magnitudes of the rates relative to each other are in the same relationship as the coefficients in the balanced equation. For example, in the combustion of propane,

$$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$$

five moles of O_2 *must* be consumed per unit of time for each mole of C_3H_8 used in the same time. Therefore, in this reaction oxygen *must* react five times faster than propane in units of mol L^{-1} s^{-1}. Similarly, CO_2 forms three times faster than C_3H_8 reacts and H_2O forms four times faster.

For expressing rate of such reactions, the rate of appearance of any reactant or rate of formation of any product is divided by their respective stoichiometric coefficients. If we know the value of a reaction rate with respect to one substance, the coefficients of the reaction's balanced equation can be used to find the rates with respect to the other substances. Consider the general reaction,

$$aA + bB \rightarrow mM + nN$$

The instantaneous rate of reaction may be defined as

$$-\frac{1}{a}\left(\frac{d[A]}{dt}\right) = -\frac{1}{b}\left(\frac{d[B]}{dt}\right) = +\frac{1}{m}\left(\frac{d[M]}{dt}\right) = +\frac{1}{n}\left(\frac{d[N]}{dt}\right) \tag{12.4}$$

where [A], [B], [M], [N] indicate the concentrations of A, B, M and N, respectively. The negative sign indicates that concentration of reactants falls as proceeds. Thus if we know the rate of formation of any one product, say M, the rest of the rates with respect to A, B and N can be determined.

For example, for the decomposition of hydrogen iodide $2HI(g) \rightarrow H_2(g) + I_2(g)$, the rate is given by

$$\text{Rate of reaction} = -\frac{1}{2}\frac{\Delta[HI]}{\Delta t} = \frac{\Delta[H_2]}{\Delta t} = \frac{\Delta[I_2]}{\Delta t}$$

Because the rates of reaction of reactants and products are all related, it does not matter which species we pick to follow concentration changes over time. In the above reaction, it is easiest to monitor the I_2 concentration because it is the only colored substance in the reaction. As the reaction proceeds, purple iodine vapor forms; there are instruments that allow us to relate the intensity of the color to the iodine concentration. Then, once we know the rate of formation of iodine, we also know the rate of formation of hydrogen. It is the same because the coefficients of H_2 and I_2 are the same. And the rate of disappearance of HI, which has a coefficient of 2 in the equation, is twice as fast as the rate of formation of I_2.

Solved Example 12-1

Use the data in the table to calculate the rate at which phenolphthalein reacts with the OH^- ion during each of the following periods.

(a) During the first time interval, when the phenolphthalein concentration falls from 0.00500 M to 0.00450 M.

(b) During the second interval, when the concentration falls from 0.00450 M to 0.00400 M.

(c) During the third interval, when the concentration falls from 0.00400 M to 0.00350 M.

Concentration of phenophthalein (M)	Time (s)
0.00500	0.0
0.00450	10.5
0.00400	22.3
0.00350	35.7
0.00300	51.1
0.00250	69.3
0.00200	91.6

Solution

The rate of reaction is equal to the change in the phenolphthalein concentration divided by the length of time over which the change occurs.

(a) During the first time period, the rate of the reaction is

$$\text{Rate} = -\frac{\Delta(X)}{\Delta t} = -\frac{(0.00450\text{ M}) - (0.00500\text{ M})}{(10.5\text{ s} - 0\text{ s})}$$

$$= 4.8 \times 10^{-5}\ \text{mol L}^{-1}\text{s}^{-1}$$

(b) During the second time period, the rate of reaction is slightly slower.

$$\text{Rate} = -\frac{\Delta(X)}{\Delta t} = -\frac{(0.00400\text{ M}) - (0.00450\text{ M})}{(22.3\text{ s} - 10.5\text{ s})}$$

$$= 4.2 \times 10^{-5}\ \text{mol L}^{-1}\text{s}^{-1}$$

(c) During the third time period, the rate of reaction is even slower.

$$\text{Rate} = -\frac{\Delta(X)}{\Delta t} = -\frac{(0.00350\ \text{M}) - (0.00400\ \text{M})}{(35.7\ \text{s} - 22.3\ \text{s})}$$
$$= 3.7 \times 10^{-5}\ \text{mol L}^{-1}\text{s}^{-1}$$

Solved Example 12-2

The following data were collected at a certain temperature for the decomposition of sulphuryl chloride, SO_2Cl_2, a chemical used in a variety of organic syntheses.

$$SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$$

Time (min)	$[SO_2Cl_2]$ (mol L^{-1})
0	0.1000
100	0.0876
200	0.0768
300	0.0673
400	0.0590
500	0.0517
600	0.0453
700	0.0397
800	0.0348
900	0.0305
1000	0.0267
1100	0.0234

Make a graph of concentration vs. time and determine the rate of formation of SO_2 at $t = 200$ min and $t = 600$ min.

Solution

Since they are in a 1-to-1 mol ratio, the rate of formation of SO_2 is equal and opposite to the rate of consumption of SO_2Cl_2. This is equal to the slope of the curve at any point on the graph (see Fig. 12.3). At 200 min, we obtain a value of about 1×10^{-4} M s^{-1}. At 600 min, this has decreased to about 7×10^{-5} M s^{-1}.

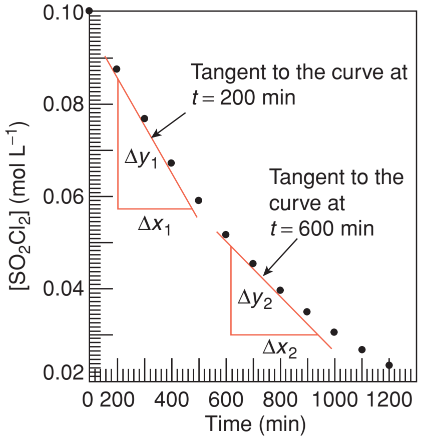


Figure 12.3

Solved Example 12-3

Explain how initial instantaneous rate of reaction can be obtained from experimental concentration versus time data.

Solution

A tangent line to the curve of concentration as a function of time at time zero is drawn. The slope of this line is determined, which is the initial instantaneous rate of reaction.

Solved Example 12-4

According to the reaction

$$Cr_2O_7^{2-} + 5H^+ + 3HNO_2 \rightarrow 2Cr^{3+} + 3NO_3^- + 4H_2O$$

The rate of disappearance of $Cr_2O_7^{2-}$ is found to be 2.4×10^{-4} mol L^{-1} s^{-1}. Find the rate of appearance of Cr^{3+} during the given time interval.

Solution

The rate of disappearance $Cr_2O_7^{2-}$ is related to the rate of appearance of Cr^{3+} by the expression

$$-\frac{d[Cr_2O_7^{2-}]}{dt} = +\frac{1}{2}\frac{d[Cr^{3+}]}{dt}$$

$$\text{or} \quad +\frac{d[Cr^{3+}]}{dt} = 2 \times 2.4 \times 10^{-4} = 4.8 \times 10^{-4}\ \text{mol L}^{-1}\ \text{s}^{-1}$$

Solved Example 12-5

The iodate ion reacts with sulphite ions in the reaction

$$IO_3^- + 3SO_3^{2-} \rightarrow I^- + 3SO_4^{2-}$$

At what rate are the iodide and sulphate ions being produced if the sulphite ion is disappearing at a rate of 2.4×10^{-4} mol L^{-1} s^{-1}?

Solution

Rate of production of $I^- = 8.0 \times 10^{-5}$ mol L^{-1} s^{-1}
Rate of production of $SO_4^{2-} = 2.4 \times 10^{-4}$ mol L^{-1} s^{-1}.

Solved Example 12-6

Hydrogen sulphide burns in oxygen to form sulphur dioxide and water. If sulphur dioxide is being formed at the rate of 0.30 mol L^{-1} s^{-1}, what are the rates of disappearance of hydrogen sulphide and oxygen?

Solution

From the coefficients in the balanced equation we see that, for every two moles of SO_2 that is produced, two moles of H_2S are consumed, three moles of O_2 are consumed, and two moles of H_2O are produced.

$$\text{Rate of disappearance of } O_2 = \left(\frac{3 \text{ mol } O_2}{2 \text{ mol } SO_2}\right)\left(\frac{0.30 \text{ mol}}{\text{L s}}\right)$$
$$= 0.45 \text{ mol L}^{-1} \text{ s}^{-1}$$

$$\text{Rate of disappearance of } H_2S = \left(\frac{2 \text{ mol } H_2S}{2 \text{ mol } SO_2}\right)\left(\frac{0.30 \text{ mol}}{\text{L s}}\right)$$
$$= 0.30 \text{ mol L}^{-1} \text{ s}^{-1}$$

12.2 | FACTORS INFLUENCING RATE OF A REACTION

The rate of reaction depends on the reaction conditions such as the temperature, concentration (pressure in case of gases) and presence of a catalyst.

1. **Nature of the reactants:** A chemical reaction involves collision of molecules resulting in the rearrangement of atoms between the reacting molecules to form products. Old bonds in the reactants are broken and new bonds are formed. Thus, the nature and the strength of the bonds in reactant molecules greatly influence the rate of its transformation into products. For example, oxidation of ferrous ion by permanganate ion in acidic medium takes place at room temperature, whereas oxidation of oxalic acid by permanganate ion in acidic medium takes place at a slightly elevated temperature. Though both reactions are of similar type, as oxalic acid requires more bonds to be broken, hence elevated temperature (heat energy) is required for the reaction to proceed.
2. **Concentration of reactants:** At a fixed temperature and in the absence of a catalyst, the rate of a given reaction increases with increase in concentration of reactants. When the concentration of the reactant is increased, the number of molecules per unit volume increases, thereby increasing the collision frequency, which ultimately causes the increase in reaction rate. The rate of a chemical reaction is the rate at which the concentrations of interacting substances vary with time. The minus sign denotes that the concentration decreases. The dependence of this rate on the concentration of reacting substances is given by the law of mass of action. In general, if dx represents an infinitesimally small change in concentration of any species during the reaction time dt, then rate may be expressed as

   $$\text{Rate} = \frac{dx}{dt}$$

   The value of dx/dt may be obtained experimentally by plotting concentration of reactant (or product) against time. The mathematical expression that relates the rate of reaction to the concentration of either reactants or products is known as the **rate law**.
3. **Temperature:** Most of chemical reactions are accelerated by increase in temperature. For example, oxidation of iron or coal is very slow at ordinary temperatures, but proceeds more rapidly at higher temperatures. In most cases, the rate of a reaction in a homogenous reaction mixture is approximately doubled or even tripled by an increase in temperature of only 10°C. In some cases, this increase in reaction rate is even higher.

4. **Surface area of the reactants:** Finely divided reactants, because of their larger surface area, react more rapidly than larger specimens of the same substance. For example, chips of wood burn faster than a log of wood.
5. **Catalysts:** Many reactions can be accelerated by the presence of small amount of substances, which themselves remain unaltered chemically during the course of reaction. Such substances are called catalysts. The action of the catalyst is specific for a reaction.
6. **Radiations:** A number of reactions register an increase in their rates, when radiations of specific wavelength are absorbed by the reacting molecules. Such reactions are called **photochemical reactions**. For example, a mixture of hydrogen and chlorine gases kept in the dark reacts, if at all, very slowly. An explosive reaction takes place when this mixture is subjected to a pulse of ultraviolet (UV) light.

$$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$$

12.3 | DIFFERENTIAL RATE EXPRESSION AND RATE CONSTANT

We have seen that the rate of reaction decreases with the passage of time as the concentration of reactants decreases. For a general reaction,

$$aA + bB \rightarrow \text{Products}$$

The rate of the reaction is expressed as

$$\text{Rate} \propto [A]^x[B]^y \tag{12.5}$$

$$\text{Rate} = k[A]^x[B]^y \tag{12.6}$$

$$-\frac{d[A]}{dt} = k[A]^x[B]^y \tag{12.7}$$

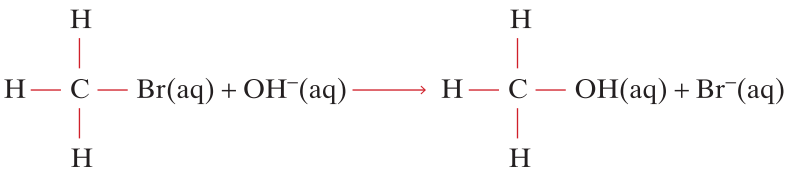
where exponents x and y may or may not be equal to the stoichiometric coefficients (a and b of the reactants). Equation (12.7) is known as **differential rate equation** and k is a constant of proportionality, known as the **rate constant**. Equation (12.5), relates rate of reaction to concentration. The expression which relates the rate of reaction to the concentration of the reactants is called **rate law** or **rate expression**. It gives the rate of reaction in terms of molar concentration of reactants with each term raised to a power, which may or may not be same as the stoichiometric coefficient of the reacting species in a balanced chemical equation.

Note: The rate describes how quickly the reactants are used up and products produced with respect to time. The rate constant is proportionality constant used in the rate law. The rate of most reactions decreases with respect to time and concentration of reactants. However, the **rate constant remains constant with respect to time and concentration**.

Sometimes the rate law is consistent with what we expect from the stoichiometry of the reaction. The balanced equation for the following reaction, for example, involves two molecules of HI, and the rate law for the reaction depends on the square of the concentration of HI.

$$2HI(g) \rightarrow H_2(g) + I_2(g); \quad \text{Rate} = k[HI]^2$$

For some reactions, however, the rate law for a reaction cannot be predicted from the stoichiometry of the reaction; it must be determined experimentally. This can be explained by the following reaction which was studied by Sir Christopher Ingold and co-workers in 1930:

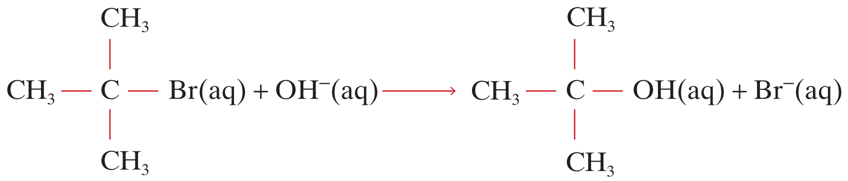


$$CH_3Br(aq) + OH^-(aq) \longrightarrow CH_3OH(aq) + Br^-(aq)$$

The rate of this reaction was found to be proportional to the concentrations of both reactants.

$$\text{Rate} = k[CH_3Br][OH^-]$$

With a similar reaction using a slightly different starting material, similar products were obtained.



$$(CH_3)_3C{-}Br(aq) + OH^-(aq) \longrightarrow (CH_3)_3C{-}OH(aq) + Br^-(aq)$$

But now the rate of reaction was proportional to the concentration of only one of the reactants.

$$\text{Rate} = k[(CH_3)_3CBr]$$

Note: It is often that the rate law does not follow the stoichiometry. For example, decomposition of N_2O_5.

Solved Example 12-7

Show that the rate law does not always follow the stoichiometry using an example.

Solution

Consider the decomposition of N_2O_5. The observed rate law for the decomposition of N_2O_5 is proportional to the concentration of N_2O_5, not to the square of the concentration of N_2O_5, as we might expect from the stoichiometry of the reaction.

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g); \quad \text{Rate} = k[N_2O_5]$$

The decomposition of N_2O_5 raises another interesting point. We can study the kinetics of this reaction by monitoring the rate at which N_2O_5 is consumed. Or we could study the rate at which NO_2 or O_2 is formed. We will get different values for the rate of reaction, however, depending on which reagent we choose. According to the balanced equation for this reaction, we get 4 mol of NO_2 for every 2 mol of N_2O_5 consumed. NO_2 is therefore formed at a rate that is twice as fast as the rate at which N_2O_5 is consumed.

$$\frac{d[NO_2]}{dt} = -2\frac{d[N_2O_5]}{dt}$$

We get only 1 mol of O_2, however, for every 2 mol of N_2O_5 consumed in this reaction. Thus O_2 is formed at a rate that is only one-half the rate at which N_2O_5 is consumed.

$$\frac{d[O_2]}{dt} = -\frac{1}{2}\frac{d[N_2O_5]}{dt}$$

Solved Example 12-8

Calculate the rate constant for the reaction between phenolphthalein and the OH^- ion if the instantaneous rate of reaction is 2.5×10^{-5} mol L^{-1} s^{-1} when the concentration of phenolphthalein is 0.00250 M.

Solution

We start with the rate law for the reaction,

$$\text{Rate} = k[\text{Phenophthalein}]$$

We then substitute the known rate of reaction and the known concentration of phenolphthalein into the equation.

$$2.5 \times 10^{-5}\ \text{mol L}^{-1}\ \text{s}^{-1} = k(0.00250\ \text{mol L}^{-1})$$

Solving for the rate constant gives the following result k = 0.010 s^{-1}. Because the rate of reaction is the change in the concentration of phenolphthalein divided by the time over which the change occurs, it is reported in units of moles per liter per second. Since the number of moles of phenolphthalein per liter is the molarity of the solution, the rate can also be reported in terms of the change in molarity per second: M s^{-1}.

Note: The units of the rate constant will depend on the form of the rate law. When substituted into the rate law, the rate constant must have units that yield a rate in units of mol L^{-1} s^{-1}.

Solved Example 12-9

The oxidation of NO (released in small amounts in the exhaust of automobiles) produces the brownish-red gas NO_2, which is a component of urban air pollution.

$$2NO + O_2 \rightarrow 2NO_2$$

The rate law for the reaction is rate = $k[NO]^2[O_2]$. At 25°C, $k = 7.1 \times 10^9$ L^2 mol^{-2} s^{-1}. What would be the rate of the reaction if [NO] = 0.0010 mol L^{-1} and $[O_2]$ = 0.034 mol L^{-1}?

Solution

Rate of reaction = 7.1×10^9 L^2 mol^{-2} $s^{-1} \times [0.0010 \text{ mol } L^{-1}]^2 \times [0.034 \text{ mol } L^{-1}] = 2.4 \times 10^2$ mol $L^{-1}s^{-1}$

12.4 | ELEMENTARY AND COMPLEX REACTIONS

A balanced chemical equation is not always a true representation of how a reaction proceeds. There are very few reactions that proceed in a single step and are known as **elementary reactions**. Elementary reactions can be two types:

1. If only one type of reactant is present, that is,

$$nA \rightarrow \text{Product(s)}$$

then the reaction is always elementary.

2. If more than one type of reactants are present, then usually coefficient of all reactants should be equal to one (unless otherwise mentioned), then such reactions are elementary.

Most of the reactions involve more than one step, that is more than one elementary reaction, and are known as **complex reactions**. Complex reactions can be expressed as a sum of elementary reactions, though this sum may not be a result of addition of unique elementary reactions. For example,

$$\text{(a)}\quad E_1 = A\text{---}C$$
$$E_2 = A + B\text{---}D$$

or

$$\text{(b)}\quad E_1 = 2A\text{---}C$$
$$E_2 = B\text{---}D$$

The sequence of reactions in a complex reaction is represented as the mechanism of reactions. The complex reactions can be of the following types.

1. **Consecutive reactions:** These are reactions taking place in a series of steps, represented as

$$A_1 \rightarrow A_2 \rightarrow A_3$$

The expression for the rate of disappearance of a reactant (or rate of appearance of a product) involves rate constants of more than a single elementary reaction.

2. **Reverse reactions:** These occur in forward and backward steps and are represented as

$$A \rightleftharpoons B$$

The rate constants of two opposing chemical reactions are involved.

3. **Parallel reactions:** In these reactions, some side reactions take place leading to the formation of some by products along with the main product. The rate of disappearance of any reactant is governed by the rate constants relating to several simultaneous reactions to form different respective products from a single set of reactants

$$\begin{array}{l} A \rightarrow B \\ \downarrow \\ C \end{array}$$

The rate laws and their derivation are discussed in a later section.

12.5 | MOLECULARITY OF A REACTION

Molecularity is defined as the total number of reacting species (molecules, atoms or ions) taking part in an elementary reaction. In other words, molecularity represents the number of reactant molecules undergoing collisions to bring about the chemical reaction. Thus in the reaction,

$$a\mathrm{A} + b\mathrm{B} \rightarrow \text{Products}$$

molecularity = $a + b$. The molecularity may be 1, 2, 3, etc., accordingly with the participation of one, two or three reactant molecules in the reaction. Depending upon this value, the reactions are classified as follows:

1. **Unimolecular reactions:** These reactions have molecularity 1. For example,

$$F_2O_2 \rightarrow F_2 + O_2$$

Note: Molecularity is defined only for elementary reactions, not for complex reaction.

2. **Bimolecular reactions:** These reactions have molecularity 2. For example,

$$2HI \rightarrow H_2 + I_2$$

$$CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$$

3. **Trimolecular or termolecular reactions:** These reactions have molecularity 3. For example,

$$2NO + Cl_2 \rightarrow 2NOCl$$

$$2NO + O_2 \rightarrow 2NO_2$$

The probability that of three molecules can reacting simultaneously is very less and hence very few examples of reactions that are trimolecular are known.

12.6 | ORDER OF A REACTION

The order of the reaction is an experimentally determined quantity and is defined with respect to a reactant as the power (exponent) of the concentration of the reactant to which the rate of the reaction is directly proportional. The overall order of the reaction is the sum of the exponents of all the reactants in the rate expression. It may be zero, positive, negative or even a fraction, say 0.5.

While considering a reaction, A → Products, suppose the rate of the reaction is (a) doubled when [A] is doubled, (b) tripled when [A] is tripled and (c) quartered when [A] is quartered; then the rate of the above reaction is proportional to first power of [A], that is

$$\text{Rate} \propto [A]$$

Suppose the rate of the above reaction is proportional to $[A]^2$, then

1. When [A] is doubled, the rate of the reaction would increase four times and
2. When [A] is tripled, the rate would increase nine times.

Therefore, rate $\propto [A]^2$. Thus, the reaction rate is dependent on the power of the concentration terms involved in rate equation, which is called the *order* of the reaction.

If a reaction involves two or more reactants, then the observed rate of the reaction would be dependent on the power of concentration terms of individual reactants, and the order would be the algebraic sum of individual power terms. For a reaction between A and B, it can be experimentally determined that the rate of the reaction relates to the concentrations of A and B as follows:

$$\text{Rate} = k[A]^a[B]^b \tag{12.8}$$

where rate is the reaction rate in mol L^{-1} s^{-1}; k is the rate constant; [A] and [B] are concentrations in mol L^{-1} of reactants A and B, respectively; a is the order with respect to A and b is the order with respect to B. This is called the *rate equation* for the reaction. The following examples illustrate the order of the reaction:

1. $2N_2O_5 \rightarrow 4NO_2 + O_2$ has Rate $= k[N_2O_5]$ and order = 1.
2. $H_2 + I_2 \rightarrow 2HI$ has Rate $= k[H_2][I_2]$ and order = 1 + 1 = 2.
3. $2NO + O_2 \rightarrow 2NO_2$ has Rate $= k[NO]^2[O_2]$ and order = 2 + 1 = 3.

For a general reaction, $aA + bB \rightarrow cC + dD$, the rate law equation is

$$\text{Rate} = k[A]^x[B]^y \tag{12.9}$$

where x and y is the order with respect to reactants A and B, respectively. Once we have found values for k, x and y, the rate law allows us to calculate the rate of the reaction at any set of known values of concentrations.

Consider, for example, the following reaction

$$H_2SeO_3 + 6I^- + 4H^+ \rightarrow Se + 2I_3^- + 3H_2O$$

Its rate law is of the form

$$\text{Rate} = k[H_2SeO_3]^x[I^-]^y[H^+]^z$$

The exponents have been found experimentally as $x = 1$, $y = 3$ and $z = 2$ for the initial rate of this reaction (i.e., the rate when the reactants are first combined). At 0°C, $k = 5.0 \times 10^5\ L^5\ mol^{-5}\ s^{-1}$. (We have to specify the temperature because k varies with it.) Substituting the exponents and the value of k into the rate law equation gives the rate law for the reaction as

$$\text{Rate} = (5.0 \times 10^5\ L^5 mol^{-5} s^{-1})[H_2SeO_3][I^-]^3[H^+]^2 \quad (\text{at } 0°C)$$

We can calculate the rate of the reaction at 0°C for any set of concentrations of H_2SeO_3, I^- and H^+ using this rate law. The overall order of a reaction may be zero or even a fraction, say 0.5. We can define that the order of the reaction with respect to a reactant is power (exponent) of the concentration of the reactant to which the rate of the reaction is directly proportional. The overall order of the reaction is the sum of the exponents of all the reactants in the rate expression.

Based on the algebraic sum of **the powers of the concentration of the reactants in the rate law**, reactions may be classified as first order, second order, third order, etc. These are as follows:

1. **Zero order reaction:** In this reaction, the value of the exponent is 0. This implies that the rate is independent of the concentration of reactants. For example, $H_2 + Cl_2 \xrightarrow{h\nu} 2HCl$ for which Rate $= k$. The rate of reaction is studied by noting the rate at which water rises in the vessel due to dissociation of HCl formed. This rate is equal to the rate of disappearance of H_2 and Cl_2. Hence, the concentration of the gases phase will not change with time, although the quantities will change.
2. **First order reaction:** In this reaction, the value of the exponent is 1. For example, $2N_2O_5 \rightarrow 4NO_2 + O_2$ for which the rate expression is Rate $= k[N_2O_5]$.
3. **Second order reaction:** In this reaction, the value of the exponent is 2. For example, $H_2 + I_2 \rightarrow 2HI$ for which the rate expression is Rate $= k[H_2][I_2]$.
4. **Third order reaction:** In this reaction, the value of the exponent is 3. For example, $2NO + O_2 \rightarrow 2NO_2$ for which the rate expression is Rate $= k[NO]^2[O_2]$.

Units of Rate Constant

From the rate law, we have

$$\frac{dx}{dt} = k[\text{Concentration of reactant}]^n$$

where dx/dt = rate of reaction, k = proportionality constant, $n = n^{th}$ order of the reaction. Therefore,

$$k = \frac{dx}{dt} \times \frac{1}{[\text{Concentration}]^n} \tag{12.10}$$

Substituting the different values of n, we can calculate units of k for zero-, first-, second- and third order reactions, as follows:

1. **Zero order reaction:** Here $n = 0$,

$$k = \left(\frac{dx}{dt}\right) \times \frac{1}{[\text{Concentration}]^0} = \text{mol L}^{-1}\ \text{time}^{-1} \tag{12.11}$$

2. **First order reaction:** Here $n = 1$,

$$k = \left(\frac{dx}{dt}\right) \times \frac{1}{[\text{Concentration}]^1} = \frac{\text{mol L}^{-1}}{\text{time}} \times \frac{1}{\text{mol L}^{-1}} = \text{time}^{-1} \tag{12.12}$$

3. **Second order reaction:** Here $n = 2$,

$$k = \left(\frac{dx}{dt}\right) \times \frac{1}{[\text{Concentration}]^2} = \frac{\text{mol L}^{-1}}{\text{time}} \times \frac{1}{(\text{mol L}^{-1})^2} = \text{L mol}^{-1}\text{time}^{-1} \tag{12.13}$$

4. **Third order reaction:** Here $n = 3$,

$$k = \left(\frac{dx}{dt}\right) \times \frac{1}{[\text{Concentration}]^3} = \frac{\text{mol L}^{-1}}{\text{time}} \times \frac{1}{(\text{mol L}^{-1})^3} = \text{L}^2\ \text{mol}^{-2}\text{time}^{-1} \tag{12.14}$$

Solved Example 12-10

The rate law for the reaction

$$2\text{NO(g)} + 2\text{H}_2\text{(g)} \rightarrow \text{N}_2\text{(g)} + 2\text{H}_2\text{O(g)}$$

is rate = $k[\text{NO}]^2[\text{H}_2]$. If the rate of reaction is 7.86×10^{-3} mol L^{-1} s^{-1} when the concentrations of NO and H_2 are both 2×10^{-6} mol L^{-1} then

(a) What is the value of the rate constant?

(b) What are the units for the rate constant? (Hint: Note the units of the reaction rate.)

Solution

(a) Using the rate law:

$$\text{Rate} = k[\text{NO}]^2[\text{H}_2]$$

Substitute in the concentration and the rate and solve for the rate constant:

$$7.86 \times 10^{-3}\text{mol L}^{-1}\text{s}^{-1} = k(2\times 10^{-6}\text{mol L}^{-1})^2 \times (2\times 10^{-6}\text{mol L}^{-1})$$

or $$k = 9.8 \times 10^{14}\ \text{L}^2\ \text{mol}^{-2}\ \text{s}^{-1}$$

(b) The units can be derived from the equation:

$$\text{mol L}^{-1}\text{s}^{-1} = k(\text{mol L}^{-1})^2(\text{mol L}^{-1})$$
$$\text{mol L}^{-1}\text{s}^{-1} = k(\text{mol}^3\text{L}^{-3})$$
$$k = \frac{\text{mol L}^{-1}\ \text{s}^{-1}}{\text{mol}^3\ \text{L}^{-3}} = \text{L}^2\text{mol}^{-2}\text{s}^{-1}$$

Solved Example 12-11

For the given reaction $\text{A} + \text{B} \rightarrow$ Products, the following data were given

Initial conc. of [A] (mol L^{-1})	0.1	0.2	0.1
Initial conc. [B] (mol L^{-1})	0.1	0.1	0.2
Initial rate (mol L^{-1} s^{-1})	0.05	0.1	0.05

(IIT-JEE 2004)

(a) Write the rate equation.

(b) Calculate the rate constant.

Solution

(a) Let the order w.r.t reactants A and B be x and y, respectively.

$$\text{Rate} = k[\text{A}]^x[\text{B}]^y$$

Putting Rate = 0.05 mol L^{-1} s^{-1}; and [A] = 0.1 mol L^{-1} and [B] = 0.1 mol L^{-1}, we get

$$0.05 = k[0.1]^x[0.1]^y \qquad (1)$$

Again putting Rate = 0.1 mol L^{-1} s^{-1}; and [A] = 0.2 mol L^{-1} and [B] = 0.1 mol L^{-1}, we

$$0.1 = k[0.2]^x[0.1]^y \qquad (2)$$

Dividing Eq. (1) by Eq. (2), we get $1 = [2]^y \Rightarrow y = 0$.

(b) The rate equation is Rate = $k[\text{A}][\text{B}]^0$. Putting Rate = 0.1 mol L^{-1} s^{-1} and [A] = 0.2 mol L^{-1}, we get

$$0.1 = k[0.2] \Rightarrow k = 0.5\ \text{s}^{-1}$$

Solved Example 12-12

Ordinary sucrose (table sugar) reacts with water in an acidic solution to produce two simpler sugars, glucose and fructose, that have the same molecular formulas.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \rightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

In a series of experiments, the following data were obtained

Initial sucrose concentrations (mol L^{-1})	Initial rate of formation of glucose (mol $L^{-1}s^{-1}$)
0.10	6.17×10^{-5}
0.20	1.23×10^{-4}
0.50	3.09×10^{-4}

(a) What is the order of the reaction with respect to sucrose?

(b) What is the value of the rate constant, with its units?

Solution

(a) When the concentration of sucrose is doubled, the rate doubles.

When the concentration of sucrose is raised five times, the rate goes up five times.

The concentration and rate are directly proportional; therefore, the reaction is first order with respect to sucrose.

(b) Now, Rate = k[Sucrose]. Substituting the given values, we get

$$(6.17 \times 10^{-5}\ \text{mol L}^{-1}\text{s}^{-1}) = k(0.10\ \text{mol L}^{-1})$$
$$\text{or} \quad k = 6.17 \times 10^{-4}\,\text{s}^{-1}$$

Therefore, the rate constant is 6.17×10^{-4} s^{-1}.

Solved Example 12-13

From the rate laws for the reactions given below, determine the order with respect to each species and the overall order:

(a) $2HCrO_4^- + 6I^- + 14H^+ \rightarrow 2Cr^{3+} + 3I_2 + 8H_2O$

Rate = $k\ [HCrO_4][I^-]^2[H^+]^2$

(b) $H_2O_2 + 2I^- + 2H^+ \rightarrow I_2 + 2H_2O$

Rate = $k\ [H_2O_2][I^-]$

Solution

(a) The order of the reaction with respect to $[HCrO_2^-]$ is 1; with respect to $[I^-]$ is 2 and with respect to $[H^+]$ is 2. The overall order of the reaction is 1 + 2 + 2 = 5.

(b) The order of the reaction with respect to $[H_2O_2]$ is 1 and with respect to $[I^-]$ is 1. The overall order of the reaction is 1 + 1 = 2.

Solved Example 12-14

For a reaction: $2P + Q \rightarrow S$; following data were collected.

	P (mol L^{-1})	Q (mol L^{-1})	Rate (mol L^{-1} min^{-1})
(a)	6×10^{-2}	1×10^{-2}	0.0012
(b)	6×10^{-2}	2×10^{-2}	0.0024
(c)	12×10^{-2}	1×10^{-2}	0.0024

Calculate the overall order of the reaction. Also find out the reaction rate constant.

Solution

The rate expression is Rate = $k[\text{P}]^x[\text{Q}]^y$.

Substituting values for (a) and (b) from the given table, and evaluating (a)/(b), we get

$$\frac{0.0012}{0.0024} = \left(\frac{1\times10^{-2}}{2\times10^{-2}}\right)^y \Rightarrow \frac{1}{2} = \left(\frac{1}{2}\right)^y \Rightarrow y = 1$$

Substituting values for (a) and (c), and evaluating (a)/(c), we get

$$\frac{0.0012}{0.0024} = \left(\frac{6\times10^{-2}}{12\times10^{-2}}\right)^x \Rightarrow \frac{1}{2} = \left(\frac{1}{2}\right)^x \Rightarrow x = 1$$

So, the overall order of the reaction is 1 + 1 = 2. Substituting values of x and y in the expression for (a), we get

$$0.0012 = k\times(6\times10^{-2})\times(1\times10^{-2}) \Rightarrow k = 2 \text{ min}^{-1}$$

Solved Example 12-15

For the reaction, $2\,NO + Cl_2 \rightarrow 2\,NOC1$ at 300 K. following data are obtained

Experiment	Initial concentration [NO]	Initial concentration [Cl_2]	Initial rate
1.	0.010	0.010	1.2×10^{-4}
2.	0.010	0.020	2.4×10^{-4}
3.	0.020	0.020	9.6×10^{-4}

Write rate law for the reaction. What is the order of the reaction? Also calculate the specific rate constant.

Solution

Let the rate law for the reaction be

$$\text{Rate} = k[NO]^x[Cl_2]^y$$

From Experiment 1, we have

$$1.2\times10^{-4} = k[0.010]^x[0.010]^y \quad (1)$$

From Experiment 2

$$2.4\times10^{-4} = k[0.010]^x[0.020]^y \quad (2)$$

Dividing Eq. (2) by Eq. (1), we get

$$\frac{2.4\times10^{-4}}{1.2\times10^{-4}} = \frac{(0.020)^y}{[0.100]^y} \Rightarrow 2 = 2^y \Rightarrow y = 1$$

From Experiment 3, we have

$$9.6\times10^{-4} = k[0.020]^x[0.020]^y \quad (3)$$

Dividing Eq. (3) by Eq. (2), we get

$$\frac{9.6\times10^{-4}}{2.4\times10^{-4}} = \frac{[0.020]^x}{[0.100]^y} \Rightarrow 4 = 2^x \Rightarrow x = 2$$

Hence, the order of the reaction = $x + y = 2 + 1 = 3$
Rate law for the reaction is

$$\text{Rate} = k[NO]^2[Cl_2]$$

Considering Eq. (1) again, we get

$$1.2\times10^{-4} = k[0.010]^2\,[0.010]$$

or
$$k = \frac{1.2\times10^{-4}}{[0.010]^3} = 1.2\times10^2 \text{ mol}^{-2}\text{ L}^2\text{ s}^{-1}$$

12.7 | CALCULATIONS OF ORDER AND MOLECULARITY BASED ON REACTION MECHANISMS

The order of a reaction needs to be determined experimentally and the definition of order of reaction is true for both elementary and complex reactions. On the other hand, molecularity of a reaction can be defined only for an elementary reaction. (Here elementary reaction means the reaction which takes place in one step.) For example,

$$H_2(g) + I_2(g) \rightarrow HI(g)$$

Here, rate = k [H_2] [I_2]. The overall order of the reaction is 2, that is, 1 with respect to [H_2] and 1 with respect to [I_2]. Since it is a one-step reaction, molecularity is 2. Thus, the order of reaction and molecularity are both 2. However, in case of complex reactions, molecularity has no meaning.

Note: The rate law for a one-step reaction agrees with the stoichiometry of the reaction.

Some important points about order and molecualrity are summarized in Table 12.1

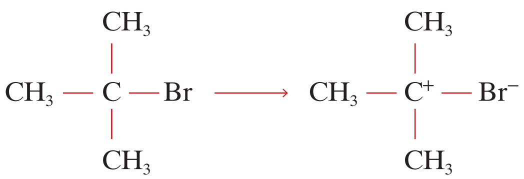
Table 12.1 Order and Molecularity

Order	Molecularity
Order of any reaction is the number of atoms or molecules which determine the rate of the reaction.	Molecularity of any reaction is the number of atoms or molecules which take part in an elementary reaction.
It may be an integer, fraction or zero.	It is always an integer.
It is an experimental quantity and varies with the conditions of the reaction.	It is a theoretical quantity that can be determined from the balanced chemical equation for an elementary reaction.
It is applicable to both elementary and complex reactions. In a complex reaction, order is given by the slowest step and the molecularity of the slowest step is the same as the overall order of the reaction.	It is applicable only to an elementary reaction and has no meaning for a complex reaction. If a complex reaction takes place in a few steps, then each step will have its molecualrity.

A balanced equation generally describes only a net overall change. Usually, however, the net change is the result of a series of simple reactions that are not at all evident from the equation. This sequence of steps by which the reactants are converted to products is **the mechanism of the reaction**. For example, the following reaction occurs in three steps.

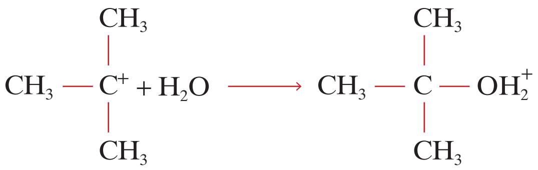
$$(CH_3)_3CBr(aq) + OH^-(aq) \rightarrow (CH_3)_3COH(aq) + Br^-(aq)$$

In the first step, the $(CH_3)_3CBr$ molecule dissociates into a pair of ions.



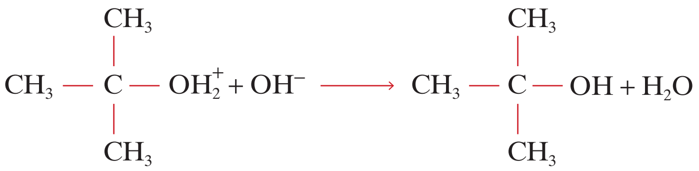
$$(CH_3)_3C{-}Br \longrightarrow (CH_3)_3C^+{-}Br^- \quad \text{(first step)}$$

The positively charged $(CH_3)_3C^+$ ion then reacts with water in a second step.



$$(CH_3)_3C^+ + H_2O \longrightarrow (CH_3)_3C{-}OH_2^+ \quad \text{(second step)}$$

The product of the reaction then loses a proton to either the OH^- ion or water in the final step.



$$(CH_3)_3C{-}OH_2^+ + OH^- \longrightarrow (CH_3)_3C{-}OH + H_2O \quad \text{(third step)}$$

The second and third steps in the reaction are much faster than the first step.

$$\begin{aligned}
&CH_3CBr \rightarrow (CH_3)_3C^+ + Br^- && \text{(slow step)}\\
&(CH_3)_3C^+ + H_2O \rightarrow (CH_3)_3COH_2^+ && \text{(fast step)}\\
&(CH_3)_3COH_2^+ + OH^- \rightarrow (CH_3)_3COH + H_2O && \text{(fast step)}
\end{aligned}$$

The overall rate of this reaction is therefore very close to the rate of the first step, that is, the slowest step. The slowest step in this reaction is called the **rate-determining step (rds)** because it literally limits the rate at which the products of the reaction can be formed. Because only one reagent is involved in the rate-limiting step, the overall rate of reaction is proportional to the concentration of only that reagent.

$$\text{Rate} = k[(CH_3)_3CBr]$$

The rate law for this reaction therefore differs from what we would predict from the stoichiometry of the reaction. Although the reaction consumes both $(CH_3)_3CBr$ and OH^-, the rate of the reaction is proportional only to the concentration of $(CH_3)_3CBr$.

Consider the example of decomposition of ozone. It decomposes according to the following reaction

$$2O_3(g) \rightarrow 3O_2(g)$$

The mechanism can be explained as

$$\text{Step 1: } O_3(g) \underset{k_{eq}}{\rightleftharpoons} O_2(g) + O(g) \qquad \text{(Fast)}$$
$$\text{Step 2: } O_3(g) + O(g) \xrightarrow[k_1]{} 2O_2(g) \qquad \text{(Slow)}$$

To find the rate expression, we consider rate determining step, which is Step 2 for this reaction. Then according to the rate law

$$\text{Rate} = k_1[O_3][O]$$

Note that in this equation, we have an intermediate [O] present. We have always to replace the intermediate in terms of known reactants and products. So from Step 1

$$k_{eq} = \frac{[O_2][O]}{[O_3]}$$

Therefore,

$$[O] = k_{eq}\frac{[O_3]}{[O_2]}$$

Substituting in rate equation, we have

$$\text{Rate} = k_1[O_3]k_{eq}\frac{[O_3]}{[O_2]} = k_1k_{eq}[O_3]^2[O_2]^{-1}$$

So the order of reaction is 1.

The series of individual steps that add up to the overall observed reaction is called the mechanism of a reaction. Each individual step in a reaction mechanism is an *elementary process* involving collisions between molecules. Information about reaction mechanisms is one of the advantages of studying rates reactions.

Note: The exponents in the rate law for an elementary process are equal to the coefficients of the reactants in the chemical equation for that elementary process. For a multistep complex reaction, the rate law for the slowest step in a mechanism should agree with the experimental rate law.

The rate laws for chemical reactions can be explained by the following general rules:

1. The rate of any step in a reaction is directly proportional to the concentrations of the reagents consumed in that step.
2. The overall rate law for a reaction is determined by the sequence of steps, or the **mechanism**, by which the reactants are converted into the products of the reaction.
3. The overall rate law for a reaction is dominated by the rate law for the slowest step in the reaction.

Note: We can tell whether a proposed mechanism is feasible if the *overall rate law derived from the mechanism agrees with the observed rate law for the overall reaction*.

Solved Example 12-16

The following reaction follows a rate which is second order with respect to NO and first order with respect to O_2. The overall order of reaction is 3.

$$2NO + O_2 \rightarrow 2NO_2$$

Write the rate equation for the reaction. If the mechanism of the reaction involves the following two steps:

$$NO_2 + O_2 \rightleftharpoons NO_3$$
$$NO + NO_3 \rightarrow 2NO_2$$

What is the molecularity of each elementary reaction and how can we deduce the rate law from these two elementary steps?

Solution

The molecularity of each elementary reaction is 2.

Let the equilibrium constant for the first elementary reaction (fast) be k and the rate constant for the second elementary reaction (slow) be k_1. Then the rate of overall reaction can be calculated as follows:

From the second elementary reaction,

$$\text{Rate } = k[NO][NO_3] \qquad (1)$$

From first elementary reaction, using law of mass action, equilibrium constant

$$K = \frac{[NO_3]}{[NO][O_2]} \Rightarrow [NO_3] = K[NO][O_2]$$

Substituting the value of $[NO_3]$ in Eq.(1), we get

$$\text{Rate } = k[NO]K[NO][O_2] = K'[NO]^2[O_2]$$

where $K' = kK$.

12.8 | PSEUDO ORDER REACTIONS

A reaction whose order is different from the actual due to large excess concentration of one of the reactants is called **pseudo-order reaction**. Consider a reaction, A + B → Products in which the reactant B is present in large excess. The rate equation can be written as:

$$\text{Rate} = k[A][B]$$

As B is present in large excess, its concentration remains practically constant in the course of the reaction. Thus, the rate law can be written as:

$$\text{Rate} = k'[A]$$

when the new rate constant $k' = k[B]$. Thus, the actual order of the reaction is second order but in practice it will be first order. Hence the reaction is said to have a pseudo-first order reaction. Some examples of pseudo-order reactions are as follows:

1. **Hydrolysis of an ester:** Ethyl acetate on hydrolysis in aqueous solution using a mineral acid as catalyst forms acetic acid and ethyl alcohol.

$$CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$$

Here a large excess of water is used and the rate law can be written as

$$\text{Rate} = k[CH_3COOH][H_2O] = k'[CH_3COOH]$$

This reaction is actually a second order reaction but, in practice, it is found to be first order. Hence it is a pseudo-first order reaction.

2. **Hydrolysis of sucrose:** Sucrose upon hydrolysis in the presence of a dilute mineral acid gives glucose and fructose.

$$C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

If large excess of water is present, its concentration is practically constant and the rate may be written as

$$\text{Rate} = k[C_{12}H_{22}O_{11}][H_2O] = k'[C_{12}H_{22}O_{11}]$$

Though the actual order is 2, its experimental order is 1. Thus it is a pseudo-first order reaction. The metabolism of hormones in human bodies is an example of pseudo-first order reactions.

Apart from pseudo first order reactions, there are reactions having molecularity greater than or equal to 3, but with order = 2. These reactions are called pseudo bimolecular reactions.

12.9 | INTEGRATED RATE EQUATIONS

While preparing some compound, we may want to know how long it will take for the reactant concentrations to drop to some particular value, so we can decide when to isolate the products. The rate law tells us how the speed of a reaction varies with the concentrations of the reactants, but not how the concentrations change over time.

The relationship between the concentration of a reactant and time can be derived from a rate law using calculus. By summing or "integrating" the instantaneous rates of a reaction from the start of the reaction until some specified time *t*, we can obtain integrated rate laws that quantitatively give concentration as a function of time. The form of the integrated rate law depends on the order of the reaction. The mathematical expressions that relate concentration and time in complex reactions can be complicated, so we will concentrate on using integrated rate laws for a few simple zero and first order reactions.

Zero Order Reactions

When the rate of a reaction does not depend on the concentration of one or more of the substances consumed in that reaction, it is said to be *zero order* in that substance. In a zero order reaction, the rate of reaction literally depends on the concentration of that reagent to the zeroth power, that is, it is independent of the concentration of the reagent. For example, decomposition of gaseous ammonia into H_2 and N_2 on a hot platinum surface. The rate at which ammonia decomposes is the same regardless of the concentration of the gas.

Consider a general zero order reaction of the type: A → Products. Let $[A]_0$ be the initial concentration of the reactant and [A] be the concentration at time *t*. The rate equation is therefore,

$$\text{Rate} = -\frac{d[A]}{dt} = k[A]_0 = k \tag{12.15}$$

or

$$d[A] = -k\,dt$$

On integration, we get

$$[A] = -kt + I \tag{12.16}$$

where *I* is the constant of integration. At $t = 0$, the concentration is $[A] = [A]_0$, therefore, substituting in Eq. (12.16), we get

$$[A]_0 = -k \times 0 + I = I$$

Substituting this value of *I* in Eq. (12.16), we get

$$[A] = -kt + [A]_0$$

or

$$k = \frac{[A]_0 - [A]}{t} \tag{12.17}$$

By definition, the quantity on RHS represents the rate of reaction. Thus, in zero order reaction, the rate constant is equal to the rate of reaction at all concentrations. The unit of rate constant is (units of concentration)/(units of time) = mol L^{-1} s^{-1}.

If the reaction is zero order, a plot of experimental data of concentration of A vs. time should fit the integrated form of the zero order rate law.

$$[A] - [A]_0 = -kt$$

or

$$k = \frac{[A]_0 - [A]}{t}$$

For the reaction A → Products, if at $t = 0$, $[\mathrm{A}]_0 = a$ and at $t = t$, $[\mathrm{A}] = a - x$, then the rate equation can be written as

$$-kt = [\mathrm{A}] - [\mathrm{A}]_0$$

$$k = \frac{[\mathrm{A}]_0 - [\mathrm{A}]}{t} = \frac{x}{t} \text{ or } x = kt$$

This equation contains two variables – [A] and t – and two constants – $[\mathrm{A}]_0$ and k. It can therefore be set up in terms of the equation for a straight line.

$$y = mx + c$$

$$[\mathrm{A}] = -kt + [\mathrm{A}]_0 \tag{12.18}$$

This equation is the integrated form of rate law for zero order reaction. If the reaction is zero order in A, a plot of the concentration of A vs. time will be a straight line with a slope equal to $-k$, as shown in Fig. 12.4 and intercept equal to $[\mathrm{A}]_0$.

For example, the decomposition of NO (or NO_2) into its elements is an important reaction because of the significant environmental problems that NO and NO_2 represent when the gases accumulate in the atmosphere. In the presence of a large excess of NO, the rate of the reaction is zero order with respect to NO.

$$\text{Rate} = k[\mathrm{NO}]^0 = k$$

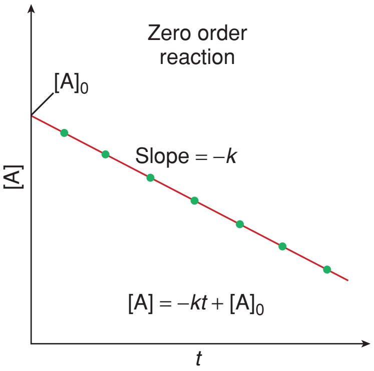


Figure 12.4 Plot of the concentration of A vs. the elapsed time since reaction started for a zero order reaction.

Note: For NO to react, it must find a site on the platinum metal at which it can bind to the metal surface. There are only a limited number of sites available at which reaction can occur, no matter how much NO is present, and only those NO molecules that occupy one of these sites can undergo a reaction. As a result, the rate of the reaction does not increase as we add more NO to the system and the reaction appears zero order with respect to NO.

First Order Reactions

Those reactions whose rate is determined by the change of only one concentration term are known as *first order reactions*. Such reactions are represented by the general reaction: A → Products.

$$\text{Rate} = -\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = k[\mathrm{A}]$$

or

$$\frac{\mathrm{d}[\mathrm{A}]}{[\mathrm{A}]} = -k\mathrm{d}t \tag{12.19}$$

where k, which is a proportionality constant, is called the velocity constant, rate constant or specific rate constant.

To deduce the integrated form of the Eq. (12.19), let us consider the initial concentration of A as $[\mathrm{A}]_0$ and the concentration of A due to reaction up to time t as [A]. Integrating Eq. (12.19), we get

$$\ln[\mathrm{A}] = -kt + I \tag{12.20}$$

where I is the constant of integration and its value can be determined easily. At $t = 0$, $[\mathrm{A}] = [\mathrm{A}]_0$, therefore above equation can be written as

$$\ln[\mathrm{A}]_0 = -k \times 0 + I = I \Rightarrow I = \ln[\mathrm{A}]_0$$

Substituting back the value of I in Eq. (12.20), we get

$$\ln[\mathrm{A}] = -kt + \ln[\mathrm{A}]_0$$

Rearranging we get,

$$\ln\frac{[\mathrm{A}]}{[\mathrm{A}]_0} = -kt \tag{12.21}$$

or

$$k = \frac{1}{t}\ln\frac{[\mathrm{A}]_0}{[\mathrm{A}]} \tag{12.22}$$

Equation (12.22) is the integrated form of rate law equation for a first order reaction. To represent the integrated law in terms of rate constant, consider the integrated rate equation at two time intervals t_1 and t_2, when the concentrations are $[\mathrm{A}]_1$ and $[\mathrm{A}]_2$, respectively, given by

$$\ln[\mathrm{A}]_1 = -kt_1 + \ln[\mathrm{A}]_0 \tag{12.23}$$

and

$$\ln[\mathrm{A}]_2 = -kt_2 + \ln[\mathrm{A}]_0 \tag{12.24}$$

Subtracting Eq. (12.23) from Eq. (12.24), we get

$$\ln[\mathrm{A}]_1 - \ln[\mathrm{A}]_2 = -kt_1 - (-kt_2)$$

$$\ln\frac{[\mathrm{A}]_1}{[\mathrm{A}]_2} = k(t_2 - t_1)$$

$$k = \frac{1}{(t_2 - t_1)}\ln\frac{[\mathrm{A}]_1}{[\mathrm{A}]_2} \tag{12.25}$$

If the reaction is first order in A, a plot of experimental data of ln A vs. time should fit the integrated form of the first order rate law.

$$\ln\frac{[\mathrm{A}]}{[\mathrm{A}]_0} = -kt$$

To see if the experimental data fits this equation, let us rearrange the integrated form of the first order rate law as follows.

$$\ln[\mathrm{A}] - \ln[\mathrm{A}]_0 = -kt$$

The equation now contains two variables – ln(A) and t – and two constants – $\ln(\mathrm{A})_0$ and k. It can therefore be set up in the form of an equation for a straight line.

$$y = mx + c$$

$$\ln[\mathrm{A}] = -kt + \ln[\mathrm{A}]_0$$

If the reaction is first order in A, a plot of the natural logarithm of the concentration of A vs. time [Fig. 12.5(a)] will be a straight line with a slope equal to $-k$ and intercept equal to $[\mathrm{A}]_0$.

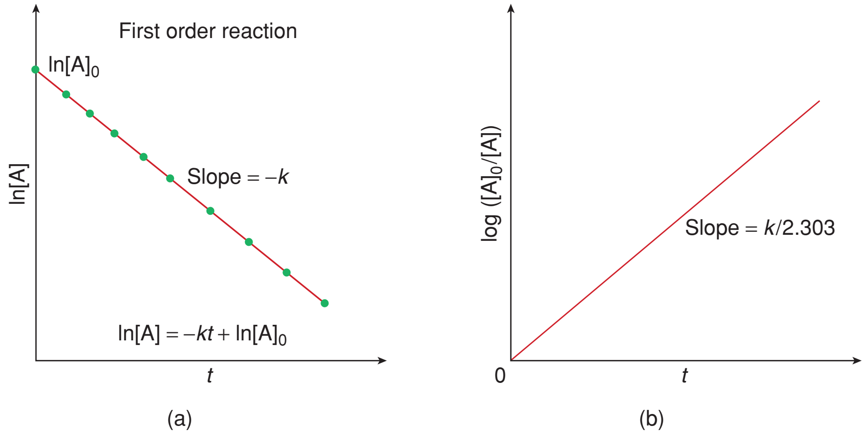


Figure 12.5 Plot of (a) ln A vs. t and (b) log $[\mathrm{A}]_0/[\mathrm{A}]$ vs. t.

The rate law equation in Eq. (12.21) can also be written as

$$k = \frac{2.303}{t}\log\frac{[\mathrm{A}]_0}{[\mathrm{A}]}$$

or

$$\log\frac{[\mathrm{A}]_0}{[\mathrm{A}]} = \frac{kt}{2.303}$$

For the reaction A → Products, if at $t = 0$, $[\mathrm{A}]_o = a$ and at $t = t$, $[\mathrm{A}] = a–x$, then the above equation can also be written as

$$\log\left(\frac{a}{a-x}\right) = \frac{kt}{2.303} \qquad (12.26)$$

where a is the initial concentration, and x is the amount reacted at time t.

The slope of plot between log $[\mathrm{A}]_0/[\mathrm{A}]$ and time t is $k/2.303$ as shown in Fig. 12.5(b). Some examples of first order reactions include:

Some examples of first order reactions include:

1. **Hydrogenation of alkenes:** $H_2C=CH_2 + H_2 \rightarrow H_3C-CH_3$.
2. **Decomposition reactions:** $SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$ and $2N_2O_5(g) \rightarrow 2N_2O_4(g) + O_2(g)$.

Solved Example 12-17

The decomposition of N_2O_5 is a first order reaction with a rate constant of 0.420 min^{-1}. If the initial concentration of N_2O_5 is 1.0 M, what will be the concentration after 5 min?

Solution

The integrated form of the rate law for reactions that follow first order kinetics is written as follows.

$$\ln\left(\frac{[\mathrm{A}]}{[\mathrm{A}]_0}\right) = -kt$$

Taking advantage of the mathematics of logarithms, we can write this equation as follows:

$$\ln[\mathrm{A}] - \ln[\mathrm{A}]_0 = -kt$$

Substituting what is known about the decomposition of N_2O_5, we obtain

$$\ln[N_2O_5] - \ln(1.0) = -(0.420\,\mathrm{min}^{-1})(5.00\,\mathrm{min})$$
$$\ln[N_2O_5] = -(0.420\,\mathrm{min}^{-1})(5.00\,\mathrm{min}) = -2.10$$
$$[N_2O_5] = 0.12\,\mathrm{M}$$

The concentration of N_2O_5, therefore, decreases by a factor of about 8 over the course of 5 min.

Solved Example 12-18

A first order reaction is 40% complete in 50 min. Calculate the value of the rate constant. In what time will the reaction be 80% complete?

Solution

For the first order reaction, $k = \dfrac{2.303}{t}\log\left(\dfrac{a}{a-x}\right)$

Given that at $t = 50$ min, $x = (40/100)\,a = 0.4a$, substituting in the equation, we get

$$k = \frac{2.303}{50}\log\left(\frac{a}{a-0.4a}\right)$$
$$= \frac{2.303}{50}\log\left(\frac{1}{0.6}\right) = 0.010216\ \mathrm{min}^{-1}$$

Solved Example 12-19

If it takes 75.0 min for the concentration of a reactant to drop to 20% of its initial value in a first order reaction, what is the rate constant for the reaction in the min^{-1}?

Solution

Assume the initial concentration is 100 and the final concentration is, therefore, 20 (the units are immaterial in this case since they will cancel out in the calculation). For a first order reaction, the integrated form of rate equation is:

$$\ln\frac{[\mathrm{A}]_0}{[\mathrm{A}]_t} = kt \Rightarrow \ln\frac{100}{20} = k(75.0\ \text{min})$$

Solving for k, we get $2.15\times10^{-2}\ \text{min}^{-1}$.

Solved Example 12-20

In designing a consumer product, it is desirable that it has a two-year shelf life. Often, this means that the active ingredient in the product should not decrease by more than 5% in two years. If the reaction is of first order, what rate constant must the decomposition reaction of the active ingredient have?

Solution

Since this is a first order reaction, then we can use the integrated rate law for a first order reaction:

$$\ln\frac{[\mathrm{A}]_0}{[\mathrm{A}]_t} = kt$$

If only 5% of the active ingredient can decompose in two years, then 95% must remain, therefore, $[\mathrm{A}]_0 = 100$, $[\mathrm{A}]_t = 95$, and $t = 2$ years. Substituting these values in integrate rate law, we get

$$\ln\frac{100}{95} = k(2) \Rightarrow k = 2.56\times10^{-2}\ \text{years}^{-1}$$

Solved Example 12-21

The rate constant for a first order reaction is $3.2\times10^{-5}\ \text{s}^{-1}$ at a particular temperature. What percentage of reactants will react on heating for 1.5 h?

Solution

For a first order reaction, the integrated rate law is given by

$$kt = \ln\frac{[\mathrm{A}]_0}{[\mathrm{A}]_t} = 2.303\log\frac{[\mathrm{A}]_0}{[\mathrm{A}]_t} \Rightarrow k = \frac{2.303}{t}\log\frac{[\mathrm{A}]_0}{[\mathrm{A}]_t}$$

Substituting the given values in the rate law equation, we get

$$3.2\times10^{-5}\ \text{s}^{-1} = \frac{2.303}{1.5\times60\times60\ \text{s}}\log\frac{a}{a-x}$$

$$\log\frac{a}{a-x} = \frac{3.2\times10^{-5}\ \text{s}^{-1}\times1.5\times60\times60\,\text{s}}{2.303} = 0.075$$

or $$\frac{a}{a-x} = 1.1885 \Rightarrow a = 1.1885a - 1.1885x$$

or $$1.1885x = 1.1885a - a = 0.1885a$$

or $$\frac{x}{a} = \frac{0.1885}{1.1885} = 0.159 = 15.9\%$$

Second Order Reactions

Reactions in which rate is determined by changing two concentration terms are known as second order reactions. These reactions may be of two types:

1. **When the reaction is 2A → Products:** In such types of reactions, two molecules of the same reactant are involved in the reaction. The rate of reaction is

$$-\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = k[\mathrm{A}]^2$$

where [A] is the concentration of reactant A. One typical example is the decomposition of hydrogen iodide, $2\mathrm{HI} \rightarrow \mathrm{H_2} + \mathrm{I_2}$. For the reaction, $2\mathrm{A} \rightarrow$ Products, if at $t = 0$, $[\mathrm{A}]_0 = a$ and at $t = t$, $[\mathrm{A}] = a - x$, then the rate constant of second order reactions having only one reactant is

$$k = \frac{1}{t}\left\{\frac{x}{a(a-x)}\right\} \tag{12.27}$$

The quantity $x/(a-x)$ is dimensionless, so units of k are (concentration)$^{-1}$ time^{-1}, that is, L mol^{-1} time^{-1}.

2. **When the reaction is A + B → Products:** In such reactions, the rate is determined by the change of two concentration terms of two different reactants.

$$-\frac{d[A]}{dt} = k[A][B] \tag{12.28}$$

where [A] and [B] are the concentration of reactants A and B, respectively, at any given time t, and k is the velocity constant. For example,

$$CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$$

For the reaction, A + B → Products, if at $t = 0$, $[A] = a$ and $[B] = b$ and at $t = t$, $[A] = a - x$ and $[B] = b - x$, then the rate constant of second order reactions having two different reactants is

$$k = \frac{1}{t}\left(\frac{2.303}{a-b}\right)\log\left(\frac{b(a-x)}{a(b-x)}\right) \tag{12.29}$$

The units of rate constant are (1/time) × (1/mol L^{-1}) × [(mol L^{-1})(mol L^{-1})/(mol L^{-1})(mol L^{-1})] = L mol^{-1} time^{-1}.

Solved Example 12-22

In a second order reaction, the reaction is found to be 25% complete in 30 min. The initial concentration of the reactant is 0.5 mol L^{-1}. Calculate **(a)** rate constant and **(b)** time required for completion of 90% of the reaction.

Solution

(a) For a second order reaction, 2A → Products, the integrated rate law equation is given by

$$kt = \frac{1}{[A]} - \frac{1}{[A]_0}$$

where $[A]_0$ is the initial concentration and [A] is the concentration at time t. When the reaction is 25% complete,

$$[A] = 75\%\ [A]_0 = 0.75\ [A]_0$$

Given that $[A]_0 = 0.5$ mol L^{-1}, therefore

$$[A] = 0.75 \times 0.5 = 0.375 \text{ mol L}^{-1}$$

Now, substituting $t = 30$ min in the integrated rate law equation, we get the rate constant as

$$k = \frac{1}{30} \times \left(\frac{1}{0.375} - \frac{1}{0.5}\right) = \frac{1}{30}(2.67 - 2)$$
$$= 0.0223 \text{ L mol}^{-1}\text{min}^{-1}$$

(b) When the reaction is 90% complete

$$[A] = 10\%[A_0] = 0.1 \times [A_0]$$

Given that $[A]_0 = 0.5$ mol L^{-1}. Therefore,

$$[A] = 0.5 \times 0.1 = 0.05 \text{ mol L}^{-1}$$

Substituting the values of k and [A] in the expression for time period, we get

$$t = \frac{1}{k}\left(\frac{1}{[A]} - \frac{1}{[A]_0}\right) = \frac{1}{0.0223}\left(\frac{1}{0.05} - \frac{1}{0.5}\right)$$
$$= \frac{1}{0.0223}(20 - 2) = 807.17 \text{ min}$$

Solved Example 12-23

A second order reaction, where $a = b$, is 20% complete in 500 s. How long will it take for the reaction to go for 60% completion?

Solution

For a second order reaction,

$$k_2 = \frac{1}{t} \times \frac{x}{a(a-x)}$$

When the reaction is 20% complete, x is 20% of the initial concentration a, that is,

$$20\% \text{ of } a = \frac{20a}{100} = 0.2a$$

So, $$k_2 = \frac{1}{500} \times \frac{0.2a}{a(a-0.2a)} = \frac{1}{200a}$$

Now suppose it takes t_1 seconds for the reaction to go for 60% completion. Then for 60% completion

$$x = \frac{60a}{100} = 0.6a$$

Thus, $$k_2 = \frac{1}{t} \times \frac{0.6a}{a(a-0.6a)} \Rightarrow \frac{1}{200a} = \frac{1}{t_1} \times \frac{3}{2a}$$

which gives $t_1 = 3000$ s.

Third Order Reactions

A third order reaction is one whose rate depends on the first power of concentration terms of three individual molecules involved in the reaction. There are three types of third order reactions:

1. **When the reaction is A + B + C → Products:** If at $t = 0$, $[A] = a$, $[B] = b$ and $[C] = c$ and at $t = t$, $[A] = a - x$, $[B] = b - x$ and $[C] = c - x$, then the third order rate equation is

$$\frac{dx}{dt} = k(a-x)(b-x)(c-x) \tag{12.30}$$

The integrated form cannot be solved easily. However, a simpler case where two of the initial concentrations are equal, that is, $a = b$, changes Eq. (12.30) to

$$\frac{dx}{dt} = k(a-x)^2(c-x) \tag{12.31}$$

Integrating Eq. (12.31), gives $$k = \left\{\frac{1}{t(c-a)^2}\right\}\left[\frac{x(c-a)}{a(a-x)} + \ln\left\{\frac{c(a-x)}{a(c-x)}\right\}\right] \tag{12.32}$$

2. **When the reaction is 2A + B → Products:** If at $t = 0$, $[A] = a$, $[B] = b$ and at $t = t$, $[A] = a - 2x$ and $[B] = b - x$, then the rate equation becomes

$$\frac{dx}{dt} = k(a-2x)^2(b-x) \tag{12.33}$$

On integration, we get $$k = \frac{1}{t(2b-a)^2}\left[\frac{2x(2b-a)}{a(a-2x)} + \ln\left\{\frac{b(a-2x)}{a(b-x)}\right\}\right] \tag{12.34}$$

3. **When the reaction is 3A → Products:** If at $t = 0$, $[A] = a$ and at $t = t$, $[A] = a - x$ then the rate equation can be written as

$$\frac{dx}{dt} = k(a-x)^3 \tag{12.35}$$

Integrating the Eq. (12.35), it gives $$k = \frac{1}{2ta^2}\left\{\frac{x(2a-x)}{(a-x)^2}\right\} \tag{12.36}$$

Higher n^{th} Order Reactions

In general, a reaction whose order is n can be written as A → Products. Let a be the initial concentration of the reactant and x be the concentration that is consumed at time, t. Then the concentration of the reactant at t is $a - x$. The rate equation is therefore,

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k(a-x)^n \Rightarrow \frac{\mathrm{d}x}{(a-x)^n} = k\,\mathrm{d}t$$

On integration, it gives $\int \frac{\mathrm{d}x}{(a-x)^n} = k\int \mathrm{d}t \Rightarrow \frac{(a-x)^{n+1}}{-n+1} = kt + I \Rightarrow \frac{1}{(a-x)^{n-1}(n-1)} = kt + I$

where I is the constant of integration. At $t = 0$, x is also equal to zero. Applying this in the above equation, it gives

$$\frac{1}{\{(a)^{n-1}(n-1)\}} = I$$

On substituting this in the above equation, we get

$$\frac{1}{(a-x)^{n-1}(n-1)} = kt + \frac{1}{(a)^{n-1}(n-1)}$$

$$kt = \frac{1}{(a-x)^{n-1}(n-1)} - \frac{1}{(a)^{n-1}(n-1)} = \frac{1}{n-1}\left[\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}}\right]$$

Replacement of Concentration Terms by other Variables in First Order Reactions

At times, in the first order reaction some other variables instead of concentration are provided. In such cases the expression $a/(a - x)$ should be obtained in terms of the known variables. Consider the following cases where concentration terms are replaced by other terms in first order reactions.

Replacement of Concentration Terms by Pressure

We know that, other variables being constant, pressure is directly proportional to the number of moles and hence the concentration. Consider the following first order reaction with the concentration terms at different time t.

	A →	B	+ C
$t = 0$	a	0	0
$t = t$	$a - x$	x	x
$t = \infty$	0	a	a

Case 1: When instead of concentration, the pressure of A at $t = 0$ and $t = t$ is given.
At $t = 0$, pressure of A is p_1 and at $t = t$, pressure of A is p_2.
Since pressure is directly proportional to concentration, therefore
Pressure at $t = 0 \propto$ concentration of A at $t = 0$, that is, $a \propto p_1$
Pressure at $t = t \propto$ concentration of A at $t = t$, that is, $(a - x) \propto p_2$
So the integrated rate equation of the first order kinetics

$$kt = 2.303\log\left(\frac{a}{a-x}\right)$$

can be written as

$$kt = 2.303\log\left(\frac{p_1}{p_2}\right)$$

Case 2: When instead of concentration, the pressure of (B + C) at $t = t$ and $t = \infty$ is given.

At $t = t$, pressure of (B + C) is p_2 and at $t = \infty$, pressure of (B + C) is p_3.
Then at $t = t$, $p_2 \propto (x+x) \Rightarrow p_2 \propto 2x$
and at $t = \infty$, $p_3 \propto (a+a) \Rightarrow p_3 \propto 2a$
Thus the concentration term can be written as

$$\frac{a}{a-x} = \frac{p_3}{p_3 - p_2}$$

Therefore, the integrated rate equation can be written as

$$kt = 2.303\log\left(\frac{p_3}{p_3 - p_2}\right)$$

Case 3: When instead of concentration, the pressure of (A + B + C) at $t = 0$ and $t = t$ is given.

At $t = 0$, pressure of (A + B + C) is p_1 and at $t = t$, pressure of (A + B + C) is p_2.
In this case, pressure of (A + B + C) ∝ concentration of (A + B + C).
At $t = 0$, $p_1 \propto (a)+(0) + (0) \Rightarrow p_1 \propto (a)$
At $t = t$, $p_2 \propto (a-x)+(x)+(x) \Rightarrow p_2 \propto (a+x)$
Therefore,

$$\frac{a}{a-x} = \frac{p_1}{2p_1 - p_2}$$

Therefore, the integrated equation for rate law is

$$kt = 2.303\log\left(\frac{p_1}{2p_1 - p_2}\right)$$

Case 4: When instead of concentration, of (A + B + C) at $t = \text{t}$ and $t = \infty$ is given.

At $t = t$, pressure of (A + B + C) is p_2 and at $t = \infty$, pressure of (A + B + C) is p_3.
Then,
At $t = t$, $p_2 \propto (a-x)+(x)+(x) \Rightarrow p_2 \propto (a+x)$
At $t = \infty$, $p_3 \propto 0 + a + \text{a}$ or $p_3 \propto 2a$
Therefore, the integrated rate law expression is

$$kt = 2.303\log\left(\frac{p_3/2}{p_3 - p_2}\right)$$

Replacement of Concentration Terms by Volume in Titrations

Consider the following first order reaction with the concentration terms at different time t;

$$\begin{array}{lcccc} & \text{A} & \xrightarrow{\text{D}} & \text{B} & + \ \text{C} \\ t=0 & a & & 0 & 0 \\ t=t & a-x & & x & x \\ t=\infty & 0 & & a & a \end{array}$$

Here A is the reactant, B and C are products and D is the catalyst.

Case 1: The oxidizing or reducing agent reacts with A only.

In this case the, concentration of A ∝ volume of oxidizing or reducing agent used.
Given that:
At $t = 0$, volume of oxidizing or reducing agent is V_1
At $t = t$, volume of oxidizing or reducing agent is V_2
Therefore, $a \propto V_1$ and $(a - x) \propto V_2$

Thus, $$\frac{a}{a-x}=\frac{V_1}{V_2}$$

Then, the integrated rate law equation is

$$kt = 2.303\log\left(\frac{V_1}{V_2}\right)$$

Case 2: The oxidizing agent or reducing agent reacts with B and C and their n-factor are in the ratio 1:1.
Given that:
At $t = t$, volume of oxidizing or reducing agent is V_2
At $t = \infty$, volume of oxidizing or reducing agent is V_3
Therefore,

$$V_2 \propto (x+x) \Rightarrow V_2 \propto 2x$$

$$V_3 \propto (a+a) \Rightarrow V_3 \propto 2a$$

Thus, $$\frac{a}{a-x}=\frac{V_3}{V_3-V_2}$$

Then the integrated rate law equation is

$$kt = 2.303\log\left(\frac{V_3}{V_3-V_2}\right)$$

Case 3: The oxidizing agent or reducing agent reacts with A, B and C and their n-factor are in the ratio 1:2: 3.
Given that:
At $t = t$, volume of oxidizing or reducing agent is V_2
At $t = \infty$, volume of oxidizing or reducing agent is V_3
Then for the reaction

	A →	B	+ C
$t = 0$	a	0	0
$t = t$	$a-x$	$2x$	$3x$
$t = \infty$	0	$2a$	$3a$

(as n –factor of A, B , C is in the ratio 1:2:3)
Therefore,

$$V_2 \propto (a-x)+(2x)+(3x) \Rightarrow V_2 \propto (a+\ 4x)$$

$$V_3 \propto (0)\ +(2a)+\ (3a) \Rightarrow V_3 \propto\ 5a$$

Thus, $$\frac{a}{a-x}=\frac{V_3/5}{(V_3-V_2)/4}$$

Then the integrated rate law equation is

$$kt = 2.303\log\left(\frac{4V_3}{5(V_3-V_2)}\right)$$

Case 4: The oxidizing agent or reducing agent reacts with A, B, C and D and the n-factor of A, B, C are in the ratio 1:1: 1.
Given that:
At $t = 0$, volume of oxidizing or reducing agent is V_1
At $t = t$, volume of oxidizing or reducing agent is V_2
At $t = \infty$, volume of oxidizing or reducing agent is V_3

Let the volume consumed by D be V_D. It will be a constant, since D is a catalyst. Then

$$V_1 \propto (a) + (0) + (0) + V_D$$

$$V_2 \propto (a-x) + (x) + (x) + V_D$$

$$V_3 \propto (0) + (a) + (a) + V_D$$

Thus,
$$\frac{a}{a-x} = \frac{V_3 - V_1}{V_3 - V_2}$$

Then the integrated rate law equation is

$$kt = 2.303 \log\left(\frac{V_3 - V_1}{V_3 - V_2}\right)$$

Replacement of Concentration Terms by Optical Rotation in Pseudo First Order Reactions

Example of inversion of cane sugar

Consider the following reaction

$$\underset{\substack{\text{Sucrose}\\ d(+)}}{C_{12}H_{22}O_{11}} + \underset{\text{Excess}}{H_2O} \rightarrow \underbrace{\underset{\substack{\text{Glucose}\\ d(+)}}{C_6H_{12}O_6} + \underset{\substack{\text{Fructose}\\ l((-)}}{C_6H_{12}O_6}}_{\text{Overall } l(-)}$$

At $t = 0$	a	0	0
At $t = t$	$a - x$	x	x
At $t = \infty$	0	a	a

The above reaction is a pseudo first order reaction as H_2O is in excess. The rate equation can be expressed as

$$k't = 2.303 \log\left(\frac{a}{a-x}\right)$$

In this reaction, dextrorotatory $d(+)$ sucrose on hydrolysis changes to a laevorotatory mixture $l(-)$ on hydrolysis. This is the reason why the reaction is called inversion of cane sugar. The optical rotation measured here is proportional to concentration of the reactants or products which are optically active, that is

$$\text{rotation}(r) \propto \text{concentration}$$

Let the proportionality constant for sucrose be l_1, glucose be l_2 and fructose be l_3.

Case 1: When instead of concentration, the optical rotation of sucrose at $t = 0$ and $t = t$ is given.

At $t = 0$, optical rotation of sucrose is r_0
At $t = t$, optical rotation of sucrose is r_t.
Then,

$$r_0 = l_1(a)$$
$$r_t = l_1(a-x)$$

Therefore,

$$\frac{a}{a-x} = \frac{r_0}{r_t}$$

Thus the integrated rate law equation is

$$k't = 2.303\log\left(\frac{r_0}{r_t}\right)$$

Case 2: When instead of concentration, the optical rotation of (sucrose + glucose + fructose) at $t = 0$, t and ∞ is given.
At $t = 0$, optical rotation of (sucrose + glucose + fructose) is r_0
At $t = t$, optical rotation of (sucrose + glucose + fructose) is r_t.
At $t = \infty$, optical rotation of (sucrose + glucose + fructose) is r_∞.
Then,

$$\begin{aligned} r_0 &= l_1(a)+l_2(0)+l_3(0) \\ r_t &= l_1(a-x)+l_2(x)+l_3(x) \\ r_\infty &= l_1(0)+l_2(a)+l_3(a) \end{aligned}$$

Therefore,

$$\frac{a}{a-x} = \frac{r_\infty - r_0}{r_\infty - r_t}$$

Thus the integrated rate law equation is

$$k't = 2.303\log\left(\frac{r_\infty - r_0}{r_\infty - r_t}\right)$$

Example of acid catalyzed hydrolysis of esters

Consider the following reaction

$$\begin{array}{llccc} & CH_3COOCH_3 + \underset{\text{excess}}{H_2O} & \xrightarrow{[H^+]} & CH_3COOH & + \; CH_3OH \\ \text{At } t=0 & a & & 0 & 0 \\ \text{At } t=t & a-x & & x & x \\ \text{At } t=\infty & 0 & & a & a \end{array}$$

This is a pseudo first order reaction as H_2O is in excess.
Given the volume of alkali (NaOH) consumed in neutralization of acid:
At $t = 0$, volume of NaOH used is V_0
At $t = t$, volume of NaOH used is V_t
At $t = \infty$, volume of NaOH used is V_∞
Here the alkali is used for neutralization of CH_3COOH present in the solution and acid used as catalyst. Let the volume consumed by catalyst be V_C. Then

$$\begin{aligned} V_0 &\propto (0)+V_C \\ V_t &\propto (x)+V_C \\ V_\infty &\propto (a)+V_C \end{aligned}$$

Therefore,

$$\frac{a}{a-x} = \frac{V_\infty - V_0}{V_\infty - V_t}$$

Then the integrated rate law equation is

$$k't = 2.303\log\frac{V_\infty - V_0}{V_\infty - V_t}$$

Solved Example 12-24

Consider a first order gas phase reaction

$$2N_2O_5(g) \rightarrow 2N_2O_4(g) + O_2(g)$$

Determine the expression for rate constant.

Solution

Let p_0 be the initial pressure of N_2O_5 and p_t be the pressure at time t. Then by Dalton's law of partial pressures,

$$p_t = p_{N_2O_5} + p_{N_2O_4} + p_{O_2}$$

At time t, let 2 mol of N_2O_5 decompose to give 2 mol of N_2O_4 and 1 mol of O_2. Let the pressure of N_2O_5 decrease by $2x$ and then the pressure of N_2O_4 and O_2 increase by $2x$ and x, respectively.

Time	N_2O_5	N_2O_4	O_2
At $t = 0$	p_t atm	0 atm	0 atm
At time t	$p_t - 2x$ atm	$2x$ atm	x atm

Then

$$p_t = (p^o - 2x) + 2x + x$$

or $$x = p_t - p^o$$

We know that $p_{N_2O_5} = p^o - 2x$. Substituting for x in the equation, we get

$$p_{N_2O_5} = p^o - 2(p_t - p^o) = 3p^o - 2p_t$$

The rate constant for the reaction can be expressed as

$$k = \frac{2.303}{t}\log\frac{p^o}{p_{N_2O_5}}$$

Substituting for $p_{N_2O_5}$, we get

$$k = \frac{2.303}{t}\log\frac{p^o}{3p^o - 2p_t}$$

Solved Example 12-25

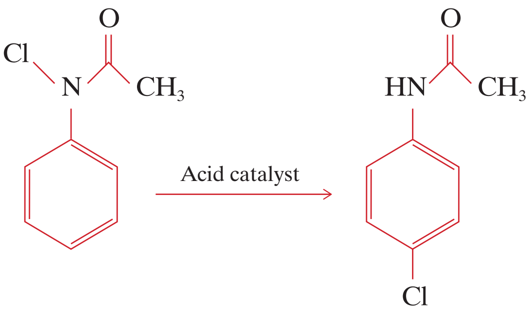
In presence of an acid N-chloro acetanilide changes slowly into p-chloro acetanilide. Former substance liberated iodine from KI and not the later and hence progress of reaction can be measured by titrating iodine liberated with $Na_2S_2O_3$ solution, the results obtained were as follows:

Time (h)	0	1	2	4	6	8
Hypo ($a - x$) (mol L^{-1})	45	32	22.5	11.3	3.7	2.9

Show that reaction is unimolecular and find out the fraction of N-chloroacetanilide decomposed after three hours.

Solution

The present reaction is:



Let us apply the kinetics of first order reaction.

Time (hour)	Rate constant (hour^{-1})
1 hour	$k = \frac{2.303}{1}\log\left\{\frac{45}{32}\right\} = 0.34098\ h^{-1}$
2 hours	$k = \frac{2.303}{2}\log\left\{\frac{45}{22.5}\right\} = 0.34660\ h^{-1}$
4 hours	$k = \frac{2.303}{4}\log\left\{\frac{45}{11.3}\right\} = 0.3455\ h^{-1}$
6 hours	$k = \frac{2.303}{6}\log\left\{\frac{45}{3.7}\right\} = 0.4164\ h^{-1}$
8 hours	$k = \frac{2.303}{8}\log\left\{\frac{45}{2.9}\right\} = 0.3428\ h^{-1}$

Average value of constant = 0.3584 h^{-1}. Since, on applying first order kinetics, we get almost same values of rate constant after different time intervals; hence, the reaction is of first order.

Let us see the fraction decomposed after 3 hours.

$$k = \frac{2.303}{t}\log\left\{\frac{a}{a-x}\right\} \Rightarrow 0.3584 = \frac{2.303}{3}\log\frac{a}{a-x}$$

Hence, the fraction decomposed, that is, x/a is

$$\frac{a}{a-x} = 2.98 \Rightarrow \frac{a-x}{a} = 0.3412$$

or $$1 - \frac{x}{a} = 0.3412 \Rightarrow \frac{x}{a} = 0.658$$

Solved Example 12-26

From the following data, show that the decomposition of hydrogen peroxide in aqueous solution is a first order reaction. What is the value of the rate constant?

Time in minutes	0	10	20	30	40
Volume (V) in mL	25.0	20.0	15.7	12.5	9.6

where V is the number of mL of potassium permanganate required to decompose a definite volume of hydrogen peroxide solution.

Solution

The equation for a first order reaction is

$$k=\frac{2.303}{t}\log\frac{a}{a-x}$$

The volume of $KMnO_4$ used evidently corresponds to the undecomposed hydrogen peroxide. Hence, the volume of $KMnO_4$ used at zero time corresponds to the initial concentration a and the volume used after time t corresponds to $(a-x)$ at that time. Inserting these values in the above equation, we get

Time (min)	Rate constant
10	$k=\frac{2.303}{10}\log\frac{25}{20.0}$ $=0.0223138\ \text{min}^{-1}=0.00372\,\text{s}^{-1}$
20	$k=\frac{2.303}{20}\log\frac{25}{15.7}$ $=0.023265\ \text{min}^{-1}=0.003871\,\text{s}^{-1}$
30	$k=\frac{2.303}{30}\log\frac{25}{12.5}$ $=0.02311\ \text{min}^{-1}=0.000385\ \text{s}^{-1}$
40	$k=\frac{2.303}{40}\log\frac{25}{9.6}$ $=0.023932\ \text{min}^{-1}=0.000398\,\text{s}^{-1}$

The constant value of k shows that the decomposition of H_2O_2, in aqueous solution is a first order reaction. The average value of the rate constant is $0.0003879\ \text{s}^{-1}$.

Solved Example 12-27

The optical rotation of sucrose in 0.5 N hydrochloric acid at 308 K and at various time intervals are given below. Find out the rate constant for the first order hydrolysis of sucrose.

Time (minutes)	0	10	20	30	60	∞
Rotation (degrees)	+32	25.5	20.0	15.5	5.0	–10.50

Solution

Here, the initial concentration $a\propto(r_0-r_\infty)$ and the concentration is x the change in time $t\propto(r_0-r_t)$. Therefore, $(a-x)\propto(r_t-r_\infty)$.
Substituting these values for different $(a-x)$ values corresponding to time t from the data in the equation for first reaction:

$$k=\frac{2.303}{t}\log\frac{a}{a-x}=\frac{2.303}{t}\log\frac{r_0-r_\infty}{r_t-r_\infty}$$

we get

(a)
$$k_1=\frac{2.303}{10}\log\frac{32-(-10.5)}{25.5-(-10.5)}$$
$$=\frac{2.303}{10}\log\frac{42.5}{36.0}=0.0166\ \text{min}^{-1}$$

(b)
$$k_1=\frac{2.303}{20}\log\frac{32-(-10.5)}{20.0-(-10.5)}$$
$$=\frac{2.303}{20}\log\frac{42.5}{30.0}=0.0166\ \text{min}^{-1}$$

(c)
$$k_1=\frac{2.303}{30}\log\frac{32-(-10.5)}{15.5-(-10.5)}$$
$$=\frac{2.303}{30}\log\frac{42.5}{26.0}$$
$$=0.0164\ \text{min}^{-1}$$

(d)
$$k_1=\frac{2.303}{60}\log\frac{32-(-10.5)}{5.0-(-10.5)}$$
$$=\frac{2.303}{60}\log\frac{42.5}{15.5}$$
$$=0.0168\ \text{min}^{-1}$$

Average value of $k_1=0.0166\ \text{min}^{-1}$.

Solved Example 12-28

1 mL of methyl acetate was added to a flask, containing 20 mL of *N*/20 HCl maintained at 25°C. Then, 2 mL of the reaction mixture was withdrawn at different intervals and titrated with a standard alkali solution. The following results were obtained.

Time (min)	0	75	119	183	∞
Alkali used (mL)	19.24	24.2	26.6	29.32	42.03

Show that the reaction follows first order kinetics.

Solution

Applying formula, we get

$$k = \frac{2.303}{t}\log\frac{V_\infty - V_0}{V_\infty - V_t}$$

where $V_\infty = 42.03$ mL and $V_0 = 19.24$ mL. Therefore, when $t = 75$ min, we have

$$k = \frac{2.303}{75}\log\frac{(42.03-19.24)}{(42.03-24.20)} = 0.00327\ \text{min}^{-1}$$

Therefore, when $t = 119$ min, we have

$$k = \frac{2.303}{119}\log\frac{(42.03-19.24)}{(42.03-26.6)} = 0.00318\ \text{min}^{-1}$$

Similarly, we can calculate k when $t = 183$ min.

$$k = \frac{2.303}{183}\log\frac{(42.03-19.24)}{(42.03-29.32)} = 0.00327\ \text{min}^{-1}$$

Since values of k are almost constant, hence proved.

Solved Example 12-29

The vapor pressure of two miscible liquids A and B are 300 mm Hg and 500 mm Hg, respectively. In a flask, 10 mol of A is mixed with 12 mol of B. However, as soon as B is added, A starts polymerizing into a completely insoluble solid. This polymerization follows first order kinetics. After 100 min, 0.525 mol of a solute is dissolved which arrests the polymerization completely. The final vapor pressure of the solution is 400 mm Hg. Estimate the rate constant of the polymerization reaction. Assume negligible volume change on mixing and polymerization, and ideal behavior for the final solution. [Given $\log_{10}11 = 1.04$].

Solution

We have $p^\circ_A = 300$ mm Hg; $p^\circ_B = 500$ mm Hg;
$n_A = 10$ mol; $n_B = 12$ mol.

Let the amount of A after 100 min is reduced to n_A. At this stage, we have

$$n_{\text{Total}} = n_A + n_B + n_{\text{Solute}} = n_A + 12 + 0.525$$

Mole fractions of A and B in the solution will be

$$x_A = \frac{n_A}{n_A + 12.525} \quad \text{and} \quad x_B = \frac{12}{n_A + 12.525}$$

Since $p_{\text{total}} = p^\circ_A x_A + p^\circ_B x_B$, we get:

$$400 = 300 \times \frac{n_A}{n_A + 12.525} + 500 \times \frac{12}{n_A - 12.525}$$

Solving for n_A, we get $n_A = 9.90$ mol.

In the reaction $nA \rightarrow A_n$ for the first order kinetics, we have:

$$kt = 2.303\log_{10}\frac{[A]_0}{[A]_t}$$

Substituting given values, we get

$$k(100\ \text{min}) = 2.303\log_{10}\frac{10}{9.9}$$

or $$k = 1.00 \times 10^{-4}\ \text{min}^{-1} = 1.67 \times 10^{-6}\ \text{s}^{-1}$$

12.10 | HALF-LIFE OF REACTIONS AND RADIOACTIVITY

The *half-life* of a reactant is a convenient way to describe how fast it reacts, particularly for a first order process. A reactant's half-life ($t_{1/2}$) is the amount of time required for half of the reactant to disappear. A rapid reaction has a short half-life because half of the reactant disappears quickly. The equations for half-lives depend on the order of the reaction and are described as follows.

1. **Zero order reactions:** For a zero order reaction, the rate constant is given by following equation. At $t = t_{1/2}$, $[\mathrm{A}] = [\mathrm{A}]_0/2$. Substituting in the above equation, we get

$$k = \frac{[\mathrm{A}]_0 - (1/2)[\mathrm{A}]_0}{t_{1/2}} \Rightarrow t_{1/2} = \frac{[\mathrm{A}]_0}{2k}$$

   Thus, the half-life time in a zero order reaction is directly proportional to the initial concentration of the reactants and inversely proportional to the rate constant.

2. **First order reactions:** When a reaction, overall, is first order, the rate constant is given by the equation

$$\ln\frac{[\mathrm{A}]_t}{[\mathrm{A}]_0} = -kt \quad \text{or} \quad \ln\frac{[\mathrm{A}]_0}{[\mathrm{A}]_t} = kt \tag{12.37}$$

   The half-life of the reactant can be obtained by setting $[\mathrm{A}]_t$ equal to one-half of $[\mathrm{A}]_0$ and time as $t_{1/2}$.

$$[\mathrm{A}]_t = \frac{1}{2}[\mathrm{A}]_0$$

   Substituting $1/2[\mathrm{A}]_0$ for $[\mathrm{A}]_t$ and $t_{1/2}$ for t in the above equation, we have

$$\ln\left(\frac{[\mathrm{A}]_0}{[\mathrm{A}]_0/2}\right) = kt_{1/2}$$

   Noting that the left-hand side of the equation simplifies to ln 2, and solving the equation for $t_{1/2}$, we have

$$t_{1/2} = \frac{\ln 2}{k} \tag{12.38}$$

   Since ln 2 equals 0.693, so Eq. (12.38) is sometimes written as

$$t_{1/2} = \frac{0.693}{k}$$

3. **Second order reactions:** Half-life period is given by $t_{1/2} = 1/ka$. Hence $t_{1/2}$ of second order reaction is inversely proportional to the initial concentration of reactant.
4. **Third order reactions:** Half-life period can be deduced as $t_{1/2} = 3/2ka^2$. It is inversely proportional to a^2.
5. **n^{th} order reactions:** The half-life period is deduced from the relation $t_{1/2} \propto \frac{1}{a^{n-1}}$. The general expression is

$$t_{1/2} = \frac{1}{k(n-1)}\left(\frac{2^{n-1}-1}{a^{n-1}}\right)$$

The expressions for rate constants and half-life time of various order reactions are listed in Table 12.2

Table 12.2 Rate constant and half-life time

Order	Expression for rate constant	Half-life (at $t = t_{1/2}$, $[\mathrm{A}] = [\mathrm{A}]_0/2$)
Zero	$k = \frac{[\mathrm{A}]_0 - [\mathrm{A}]}{t}$	$k = \frac{[\mathrm{A}]_0 - (1/2)[\mathrm{A}]_0}{t_{1/2}} \Rightarrow t_{1/2} = \frac{[\mathrm{A}]_0}{2k}$
First	$\ln\frac{[\mathrm{A}]_0}{[\mathrm{A}]_t} = kt$	$\ln\left(\frac{[\mathrm{A}]_0}{[\mathrm{A}]_0/2}\right) = kt_{1/2} \Rightarrow t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$
Second	$kt = \ln\frac{1}{[\mathrm{A}]} - \frac{1}{[\mathrm{A}]_0}$ (for the same reactant)	$t_{1/2} = \frac{1}{k}\ln\frac{1}{[\mathrm{A}]_0/2} - \frac{1}{[\mathrm{A}]_0} \Rightarrow \frac{1}{k[\mathrm{A}]_0}$
Third	$kt = \frac{1}{2[\mathrm{A}]_0^2}\left[\frac{([\mathrm{A}]_0 - [\mathrm{A}])(2[\mathrm{A}]_0)}{[\mathrm{A}]_0^2}\right]$ (for the same reactant)	$\frac{3}{2}k[\mathrm{A}]_0^2$

Radioactivity

Radioactivity is an emission of particles and/or electromagnetic radiation by unstable atomic nuclei. The stream of particles (photons coming from the sample is called nuclear) atomic radiation and the phenomena is called radioactivity. To understand the concept of radioactive decay and the half-life time of radioactive isotopes let us consider carbon-14 (^{14}C), a radioactive isotope that is formed in small amounts in the upper atmosphere by the action of cosmic rays on nitrogen atoms. Once formed, it diffuses into the lower atmosphere. It becomes oxidized to carbon dioxide and enters the earth's biosphere by means of photosynthesis. ^{14}C thus gets incorporated into plant substances and into the materials of animals that eat plants. As the ^{14}C decays, more is ingested by the living thing. The net effect is an overall equilibrium involving ^{14}C in the global system. As long as the plant or animal is alive, its ratio of ^{14}C atoms to ^{12}C atoms is constant. At death, an organism's remains have as much ^{14}C as they can ever have, and they now slowly lose this ^{14}C by decay.

Let us use the integrated form of the equation for a first order reaction to calculate how long it would take for the ^{14}C in a piece of charcoal to decay to half of its original concentration. All radioactive decay processes are first order. Therefore, ^{14}C decays by first order kinetics.

$$\text{Rate} = k[^{14}\text{C}]$$

The experimental value for the rate constant for this reaction is 1.210×10^{-4} years^{-1}. The integrated form of the rate law for this reaction would be written as follows:

$$\ln\left(\frac{[^{14}\text{C}]}{[^{14}\text{C}]_0}\right) = -kt_{1/2}$$

But we are interested in the moment when the concentration of ^{14}C in the charcoal is half of its initial value $[^{14}\text{C}] = [^{14}\text{C}]_0/2$. Substituting this relationship into the integrated form of the rate law gives the following equation:

$$\ln\left(\frac{[^{14}\text{C}]_0/2}{[^{14}\text{C}]_0}\right) = -kt_{1/2}$$

We now simplify the equation as follows:

$$\ln\left(\frac{1}{2}\right) = -kt_{1/2}$$

and then solve for $t_{1/2}$ as

$$t_{1/2} = -\frac{\ln(1/2)}{k} = \frac{0.6931}{1.210 \times 10^{-4}\ \text{years}^{-1}} = 5730 \text{ years}$$

It, therefore, takes 5730 years for half the amount of the ^{14}C in the sample to decay. This is called the **half-life** ($t_{1/2}$) of ^{14}C.

Solved Example 12-30

Which radioactive isotope would have the longer half-life ^{15}O or ^{19}O? Given that

For ^{15}O, $k = 5.63 \times 10^{-3}\ s^{-1}$

For ^{19}O, $k = 2.38 \times 10^{-2}\ s^{-1}$

Solution

The rate constant for the decay of ^{15}O is less than that for ^{19}O. Therefore, the rate of decay of ^{15}O will be slower and it will have a longer half-life.

Solved Example 12-31

Suppose a patient is given a certain amount of iodine-131 (^{131}I) as part of a diagnostic procedure for a thyroid disorder. Given that the half-life of radioactive ^{131}I is 8.0 days, what fraction of the initial ^{131}I would be present in a patient after 24 days if none of it were eliminated through natural body processes?

Solution

We know that radioactive ^{131}I decays by a first order process with a constant half-life. A period of 24 days is exactly three 8.0 day half-lives. Therefore, let us apply the half-life concept three times. If we take the fraction initially present to be 1, we can set up a table

Half-life	0	1	2	3
Fraction	1	1/2	1/4	1/8

Half of the ^{131}I is lost in the first half-life, half of that disappears in the second half-life, and so on. Therefore, the fraction remaining after three half-lives is 1/8. The fraction remaining after n half-lives is $(1/2)^n$, or simply $1/2^n = 1/8$.

Alternate solution

We could also have solved the problem using the integrated first order rate law equation. We will need the first order rate constant, k, which we can obtain from the half-life by:

$$k = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{8.0\ \text{days}} = 0.0866\ \text{days}^{-1}$$

Then we can use the integerated rate law equation to compute the fraction $[A]_0/[A]_t$.

$$\ln\frac{[A]_0}{[A]_t} = kt = (0.0866\ \text{days}^{-1})(24.0\ \text{days}) = 2.08$$

Taking the antilog of both sides, we have

$$\frac{[A]_0}{[A]_t} = e^{2.08} = 8.0$$

The initial concentration, $[A]_0$, is 8.0 times as large as the concentration after 24.0 days, so the fraction remaining after 24 days is 1/8, which is exactly what we obtained much more simply above.

Solved Example 12-32

Calculate the rate constant for the following acid–base reaction if the half-life for the reaction is 0.0282 s at 25°C and the reaction is first order in the NH_4^+ ion.

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$$

Solution

For a first order reaction,

$$\text{Half-life } (t_{1/2}) = \frac{\ln 2}{k} = \frac{0.693}{k}$$

Substituting the given value of k in the equation, we get

$$0.0282\ \text{s} = \frac{0.693}{k} \Rightarrow k = \frac{0.693}{0.0282}\ \text{s}^{-1} = 24.574\ \text{s}^{-1} \approx 24.6\ \text{s}^{-1}$$

Solved Example 12-33

The half-life of first order decomposition of nitramide is 2.1 h at 15°C.

$$NH_2NO_2(aq) \rightarrow N_2O(g) + H_2O(l)$$

If 6.2 g of NH_2NO_2 is allowed to decompose, find the

(a) time taken for nitramide to decompose 99%.

(b) volume of dry N_2O gas produced at this point at STP.

Solution

(a) Using first order kinetics, we have:

$$kt = 2.303\log_{10}\frac{C_0}{C_t} \Rightarrow \frac{0.693}{2.1}\times t$$

$$= 2.303\log_{10}\left(\frac{100}{100-99}\right) \Rightarrow t = 13.95\ \text{h}$$

(b) 6.2 g of $NH_2NO_2 \equiv 0.1$ mol. From the reaction, we have

	$NH_2NO_2(aq)$	$\rightarrow N_2O(g)$	$+ H_2O(l)$
Initial moles	0.1	0	0
Moles at $t = 13.95$ h	$0.1 - 0.99\times 0.1$	0.99×0.1	0.99×0.1

Therefore, moles of $N_2O = 0.099$, or volume of N_2O at STP is

$$V_{N_2O} = 0.99\times 22.4 = 2.217\ \text{L}$$

Solved Example 12-34

For the reaction $2X(g) \rightarrow 3Y(g) + 2Z(g)$

Time (min)	0	100	200
Partial pressure of X (mm Hg)	800	400	200

Assuming ideal gas condition, calculate **(a)** order of reaction, **(b)** rate constant, **(c)** time taken for 75% completion of reaction and **(d)** total pressure when $p_X = 700$ mm Hg.

(IIT-JEE 2005)

Solution

(a) From the given data, it is observed that $t_{1/2}$ of the X is constant, that is, 100 min. So, the order of the reaction is 1.

(b) Rate constant $(k) = \dfrac{0.693}{t_{1/2}} = \dfrac{0.693}{100} = 6.93 \times 10^{-3}\ \text{min}^{-1}$

(c) Time taken for 75% completion of reaction $t = 2 \times t_{1/2} = 2 \times 100 = 200$ min.

(d) The reaction can be represented as

	$2X(g) \rightarrow$	$3Y(g)$ +	$2Z(g)$
Initial pressure	800	0	0
Pressure at time t	$800 - x$	$(3/2)x$	x

Given that $800 - x = 700$ mm Hg, so $x = 100$ mm Hg

Hence, the total pressure = 700 + 150 + 100 = 950 mm Hg.

Solved Example 12-35

The half-life of a radioactive isotope is 3.0 h. What mass of it remains undecayed in 15 h if the initial mass of the isotope was 100 g?

Solution

Given that $t_{1/2} = 3.0$ h, so $k = 0.693/3 = 0.231\ \text{h}^{-1}$. Also, given that $a = 100$ g. Therefore, using first order kinetics, we have

$$kt = 2.303 \log\left(\frac{a}{a-x}\right)$$

Substituting values, we get

$$15 = \frac{2.303}{0.231}\log\left(\frac{100}{100-x}\right)$$

or $$\log\left(\frac{100}{100-x}\right) = \frac{15 \times 0.231}{2.303} = 1.5045$$

or $$\left(\frac{100}{100-x}\right) = \text{antilog}(1.5045) = 31.95$$

or $$100 - x = \frac{100}{31.95} \Rightarrow x = 96.87\ \text{g}$$

Solved Example 12-36

In an ore containing uranium, the ratio of ^{238}U to ^{206}Pb nuclei is 3. Calculate the age of the ore, assuming that all the lead present in the ore is the final stable product of ^{238}U. The half-life of ^{238}U is 4.5×10^9 years.

Solution

The radioactive decay follows first order kinetics. Here, we take $[A]_0 \equiv N_0$ and $[A]_t = N_t$ and $k \equiv \lambda$. The first order rate equation for radioactive decay is:

$$\lambda t = 2.303\ \log\frac{N_0}{N_t}$$

where λ the decay constant or distingeration constant = $0.693/t_{1/2}$; N_0 = initial nuclei (i.e., at $t = 0$); N_t = nuclei at $t = t$. For the radioactive reaction, we have

$$\begin{array}{lcl} & U^{231} \rightarrow & Pb^{206} \\ & N_0 \equiv x & 0 \\ & N_t \equiv x - y & y \end{array}$$

Therefore, $$\frac{N_0}{N_t} = \frac{x}{x-y}$$

We use the expression $\lambda t = 2.303\ \log_{10}\dfrac{x}{x-y}$. Given that $(x-y)/y = 3$, so

$$\frac{x}{y} - 1 = 3 \Rightarrow \frac{x}{y} = 4 \Rightarrow \frac{y}{x} = \frac{1}{4} \Rightarrow \frac{x-y}{x} = \frac{3}{4} \Rightarrow \frac{x}{x-y} = \frac{4}{3}$$

Substituting, we get

$$t = \frac{2.303}{0.693} \times 4.5 \times 10^9\ \log_{10}\frac{4}{3} = 1.85 \times 10^9\ \text{years}$$

Solved Example 12-37

During nuclear explosion, one of the products is ^{90}Sr with half-life of 28.1 years. If 1 μg of ^{90}Sr was absorbed in the bones of a newly born baby instead of calcium, how much of it will remain after 10 years and 60 years if it is not lost metabolically?

Solution

The half-life of ^{90}Sr is $t_{1/2} = 28.1$ years. Given that the initial amount of ^{90}Sr absorbed, $a = 1$ μg; we need to calculate the final amount of ^{90}Sr left in the body $a_t = ?$ For the reaction,

$$k = \frac{6.93}{t_{1/2}} = \frac{0.693}{28.1\,\text{years}} \text{ and } k = \frac{2.303}{t}\log\frac{a}{a_t}$$

(a) Time $t = 10$ years, then

$$\frac{0.693}{28.1\,\text{years}} = \frac{2.303}{10\,\text{years}}\log\frac{1\,\mu\text{g}}{a_t}$$

$$\log\frac{1\,\mu\text{g}}{a_t} = \frac{0.693\times 10}{28.1\times 2.303} = 1.1071 \Rightarrow \frac{1\,\mu\text{g}}{a_t} = 1.2796$$

or $$a_t = \frac{1\,\mu\text{g}}{1.2796} = 0.78\,\mu\text{g}$$

(b) Time $t = 60$ years, then

$$\frac{0.693}{28.1} = \frac{2.303}{60}\log\frac{1\,\mu\text{g}}{a_t} \Rightarrow \log\frac{1\,\mu\text{g}}{a_t}$$

$$= \frac{0.693\times 60}{28.1\times 2.303} = 0.6425$$

So, $$\frac{1\,\mu\text{g}}{a_t} = 4.39 \Rightarrow a_t = \frac{1\,\mu\text{g}}{4.39} = 0.228\,\mu\text{g}$$

Solved Example 12-38

The half-life of first order decomposition of nitramide is 2.1 h at 15°C.

$$NH_2NO_2(s) \rightarrow N_2O(g) + H_2O(l)$$

If 6.2 g of NH_2NO_2 is allowed to decompose, calculate **(a)** time taken for NH_2NO_2 to decompose 99% and **(b)** volume of dry N_2O produced at this point measured at STP.

Solution

For a first order reaction, rate constant expression is

$$k = \frac{2.303}{t}\log\frac{[A]_0}{[A]_t} \text{ where } k = \frac{0.693}{t_{1/2}} = \frac{0.693}{2.1}$$

and $[A]_t = 0.001$ mol L^{-1}. The initial moles of nitramide is

$$[A]_0 = \frac{6.2}{62} = 0.1\text{ mol L}^{-1}$$

and time is

$$t = \frac{2.303\times 2.1}{0.693}\log\frac{0.1}{0.001} = 13.95\text{ h}$$

Since, the decomposition is 99%, so 99% of the initial moles of NH_2NO_2 would be converted to N_2O.

$$\text{Moles of } N_2O = \frac{0.1\times 99}{100}$$

$$\text{Volume of } N_2O \text{ at STP} = \frac{0.1\times 99\times 22.4}{100} = 2.217\text{ L}$$

12.11 | DERIVATION OF RATE LAWS FOR COMPLEX REACTIONS USING INTEGRATED RATE EQUATIONS

Consecutive or Sequential Reactions

These reactions proceed from reactants to final products through one or more intermediate stages. The overall reaction is a result of several successive or consecutive steps.

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

If the rate of reactions is k_1 and k_2, then the reaction rate is

$$\frac{d[A]}{dt} = k_1[A] \qquad \frac{d[B]}{dt} = k_1[A] - k_2[B] \qquad \frac{d[C]}{dt} = k_2[B]$$

The integrated rate equation for [A] is

$$[\mathrm{A}] = [\mathrm{A}]_0 e^{-k_1 t}$$

Now,

$$\frac{\mathrm{d[B]}}{\mathrm{d}t} = k_1[\mathrm{A}]_0 e^{-k_1 t} - k_2[\mathrm{B}]$$

The solution of this equation is

$$[\mathrm{B}] = \frac{k_1}{k_2 - k_1}[\mathrm{A}]_0 (e^{-k_1 t} - e^{-k_2 t})$$

Since by mass balance, $[\mathrm{C}] = [\mathrm{A}]_0 - [\mathrm{B}] - [\mathrm{A}]$, so

$$[\mathrm{C}] = [\mathrm{A}]_0 \left\{ 1 - \frac{k_1}{k_2 - k_1}(e^{-k_1 t} - e^{-k_2 t}) - e^{-k_1 t} \right\}$$

Note: Steady state approximation implies that the steady state has been achieved and there is no further change in the activity of the species on which this approximation is applied. In the following reaction

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \xrightarrow{k_2} \mathrm{C}$$

If we apply steady state approximation for B, then

$$\frac{\mathrm{d(B)}}{\mathrm{d}t} = 0 = k_1[\mathrm{A}] - k_2[\mathrm{B}]$$

Therefore,

$$[\mathrm{B}] = \frac{k_1}{k_2}[\mathrm{A}] = \frac{k_1}{k_2 - k_1}[A]_0 (e^{-k_1 t} - e^{-k_2 t})$$

Then

$$\frac{\mathrm{d(B)}}{\mathrm{d}t} = 0 = -k_1 e^{-k_1 t} - (-k_2) e^{-k_2 t}$$

$$\frac{k_2}{k_1} = e^{(k_1 - k_2)t}$$

Therefore, the time at which concentration of B is the maximum is given by

$$t_{\max} = \frac{\ln(k_2 / k_1)}{(k_2 - k_1)}$$

Case 1: When $k_1 \gg k_2$: In this case, we can observe that the reaction $\mathrm{A} \xrightarrow{k_1} \mathrm{B}$ occurs first and goes nearly to completion before the reaction $\mathrm{B} \xrightarrow{k_2} \mathrm{C}$ takes place. Thus, nearly all the A is converted to the intermediate B before any appreciable conversion of B to C occurs. Thus,

$$[\mathrm{B}] = [\mathrm{A}]_0 (e^{-k_1 t} - e^{-k_2 t})$$

Since $k_1 \gg k_2$, the second term in the parentheses rapidly approaches zero while the first term is still near unity. Consequently, the concentration of the intermediate B rapidly reaches a value nearly equal to $[\mathrm{A}]_0$ and then during most of the reaction, B decays slowly according to the equation $[\mathrm{B}] = [\mathrm{A}]_0 e^{-k_2 t}$. The exact solution for $k_1 = 10\, k_2$ is shown in Fig. 12.6(a).

Case 2: When $k_2 \gg k_1$: In this case concentration of B is given as

$$[\mathrm{B}] = \frac{k_1}{k_2}[\mathrm{A}]_0(e^{-k_1 t} - e^{-k_2 t})$$

Since $k_2 \gg k_1$, the second term in the parentheses rapidly approaches zero while the first term is still near unity. Consequently, the concentration of B rapidly approaches $\frac{k_1}{k_2}[\mathrm{A}]_0$ and then decays more slowly according to

$$[\mathrm{B}] = \frac{k_1}{k_2}[\mathrm{A}]_0\, e^{-k_1 t}$$

Since, k_1/k_2 is very small, the maximum concentration of B is much less than $[\mathrm{A}]_0$. Figure 12.6(b) shows the exact concentrations for $k_2 = 10\,k_1$

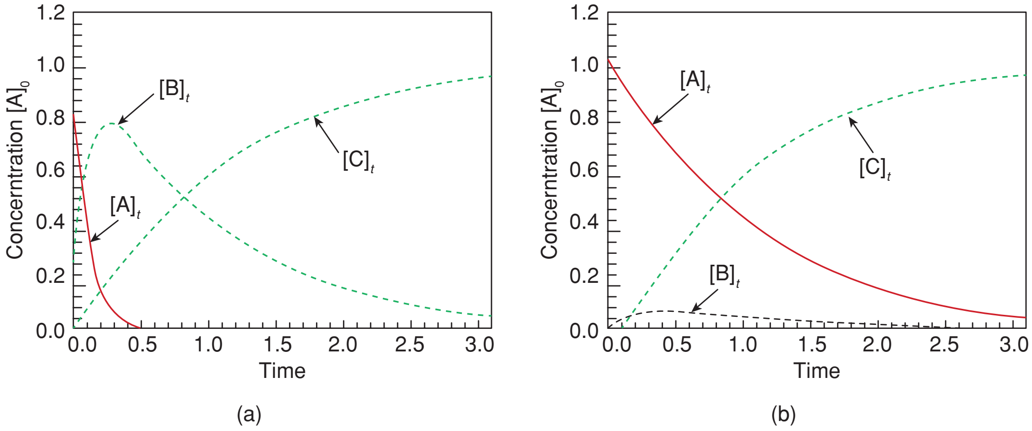


Figure 12.6 Concentrations in a consecutive reaction when (a) $k_1 = 10k_2$ and (b) $k_2 = 10k_1$.

Some examples of consecutive reactions are:

1. The pyrolysis of acetone

$$(\mathrm{CH_3})_2\mathrm{CO} \rightarrow \mathrm{CH_4} + \underset{\text{Ketene}}{\mathrm{CH_2{=}C{=}O}}$$

$$\mathrm{CH_2{=}C{=}O} \rightarrow \mathrm{C_2H_4} + \mathrm{CO}$$

2. Decomposition of ethylene oxide

$$(\mathrm{CH_2})_2\mathrm{O} \xrightarrow{k_1} \mathrm{CH_3CHO}$$

$$\mathrm{CH_3CHO} \xrightarrow{k_2} \mathrm{CO} + \mathrm{CH_4}$$

Solved Example 12-39

For the reaction $\mathrm{A} \xrightarrow{k_1 = 0.1\ \mathrm{s^{-1}}} \mathrm{B} \xrightarrow{k_2 = 1/30\ \mathrm{s^{-1}}} \mathrm{C}$, find the time at which concentration of B is maximum. Also, find the concentration of A, B and C at this instant. Take $[\mathrm{A}]_0 = 1$ M.

Solution

The time at which [B] is maximum is

$$t = \frac{1}{k_2 - k_1}\ln\frac{k_2}{k_1} = \frac{1}{0.1 - 1/30}\ln\frac{0.1}{1/30} = 15\ln 3$$

The concentration of A at that time is

$$[\mathrm{A}]_{t=15\ln 3} = [\mathrm{A}]_0 e^{-k_1 t} = 1 \times e^{-0.1\times 15\ln 3}$$

$$= e^{\ln(3^{-1.5})} = 3^{-1.5} = \frac{1}{3\sqrt{3}}\ \mathrm{M}$$

When [B] is maximum,

$$k_1[\mathrm{A}] = k_2[\mathrm{B}]_{\max}\left(\frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t}=0\right)$$

or
$$\frac{1}{10}\times\frac{1}{3\sqrt{3}} = \frac{1}{30}[B]_{\max}$$

$$\Rightarrow [B]_{\max} = \frac{1}{\sqrt{3}}M$$

Also $[\mathrm{A}]+[\mathrm{B}]+[\mathrm{C}]=[\mathrm{A}]_0$, so

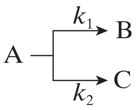
$$[\mathrm{C}] = 1-\frac{1}{3\sqrt{3}}-\frac{1}{\sqrt{3}} = 1-\frac{4}{3\sqrt{3}}\mathrm{M}$$

Thus, the reaction can be represented as

$$\mathrm{A}\xrightarrow{k_1=0.1\ \mathrm{s}^{-1}}\mathrm{B}\xrightarrow{k_2=1/30\ \mathrm{s}^{-1}}\mathrm{C}.$$

Parallel Reactions

In these reactions, some side reactions take place leading to the formation of some byproducts along with the main product. These reactions can be explained as follows:



The reactant A reacts to give products B and C separately by following two different reaction pathways involving different rate constants k_1, k_2, respectively.

Then:

$$\%\text{ age of B} = \frac{k_1}{k_1+k_2}\times 100 \qquad \%\text{ age of C} = \frac{k_2}{k_1+k_2}\times 100$$

If $k_1 \gg k_2$ then $\mathrm{A}\rightarrow\mathrm{B}$ is the main reaction and $\mathrm{A}\rightarrow\mathrm{C}$ is the side reaction. The reactions $\mathrm{A}\rightarrow\mathrm{B}$ and $\mathrm{A}\rightarrow\mathrm{C}$, with rate constants k_1 and k_2 will have rate equations

$$-\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = (k_1+k_2)[\mathrm{A}] \quad \frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} = k_1[\mathrm{A}] \quad \frac{\mathrm{d}[\mathrm{C}]}{\mathrm{d}t} = k_2[\mathrm{A}]$$

Thus, the disappearance of A will be of first order, and on the basis of the earlier discussion of first order reactions we can derive equations for the concentrations of B and C as functions of time as they are produced in the parallel reactions.

We can write
$$[\mathrm{A}] = [\mathrm{A}]_0 e^{-(k_1+k_2)t}$$

The rate equation for B is
$$\frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} = k_1[\mathrm{A}] = k_1[\mathrm{A}]_0 e^{-(k_1+k_2)t}$$

Integration yields
$$[\mathrm{B}] = \frac{-k_1[\mathrm{A}]_0}{(k_1+k_2)}e^{-(k_1+k_2)t} + \text{constant}$$

If $[\mathrm{B}]=0$ at $t=0$, the constant is $k_1[\mathrm{A}]_0/(k_1+k_2)$ and

$$[\mathrm{B}] = \frac{k_1[\mathrm{A}]_0}{(k_1+k_2)}[1-e^{-(k_1+k_2)t}]$$

Thus, the fraction of A that is converted to at infinite time is $k_1\ (k_1+k_2)$. At any time the sum of [A], [B] and [C] must be equal to the total concentration of A at the beginning, $[\mathrm{A}]_0$. Consequently, if $[\mathrm{C}]_0 = 0$, then

$$[\mathrm{C}] = \frac{k_2[\mathrm{A}]_0}{(k_1+k_2)}[1-e^{-(k_1+k_2)t}]$$

It is apparent from these equations that the ratio of the concentrations of B and C is always given by k_1/k_2, which is referred to as the branching ratio.

Thus, both B and C rise exponentially with a rate constant equal to $[k_1 + k_2]$, as shown in Fig. 12.7.

The reason for this behavior is that the rates of production of both B and C depend on the concentration of A, which decreases exponentially with a rate constant equal to the sum $[k_1 + k_2]$. The ratio of products, called the branching ratio, is at all times.

$$\frac{[\mathrm{B}]}{[\mathrm{C}]} = \frac{k_1}{k_2}$$

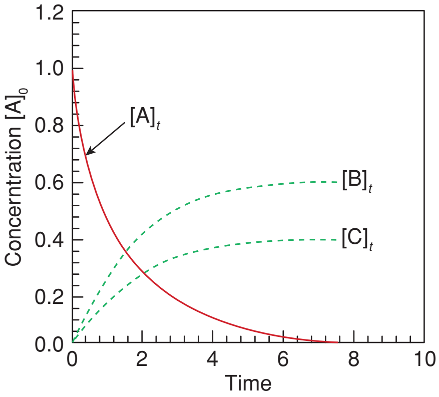
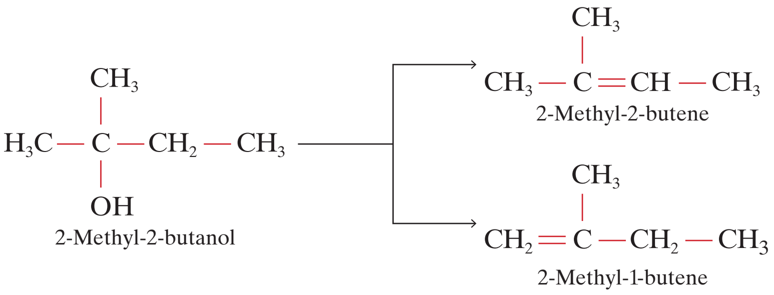


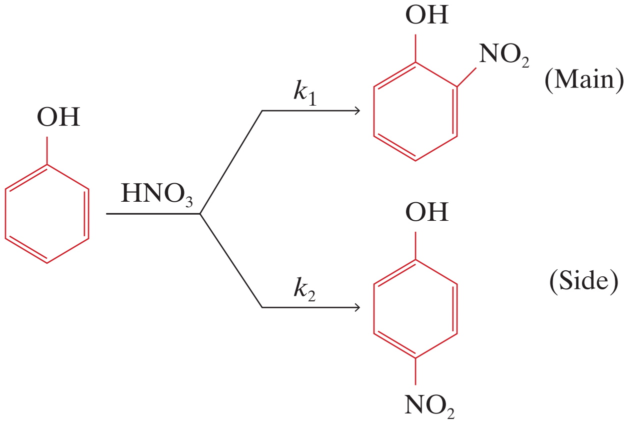
Figure 12.7 Concentrations are a function of time for the parallel reactions.

Thus, while the magnitude of [B] relative to [C] is constant and not generally unity, the rate constant $[k_1 + k_2]$ with which each concentration approaches its final value is the same for both [B] and [C].
Some examples of parallel reactions are:

1. Dehydration of 2-methyl-2-butanol:

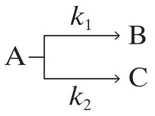


2. Nitration of phenol:



Solved Example 12-40

Consider the following reaction path followed by A:



Calculate [C] after 3 h of the reaction if $[\mathrm{A}]_0 = 0.01$ mol L^{-1}. Also given that $k_1 = 2.0 \times 10^{-5}\ \mathrm{s}^{-1}$ and $k_2 = 4.0 \times 10^{-5}\ \mathrm{s}^{-1}$.

Solution

The rate constant for the reaction is $k = k_1 + k_2 = 2.0 \times 10^{-5} + 4.0 \times 10^{-5} = 6.0 \times 10^{-5}\ \text{s}^{-1}$. From first order kinetics, we have

$$kt = 2.303 \log \frac{[\text{A}]_0}{[\text{A}]_t}$$

Substituting values, we get

$$6 \times 10^{-5} \times 3 \times 60 \times 60 = 2.303 \log \frac{0.25}{[\text{A}]_t} \Rightarrow \frac{0.25}{[\text{A}]_t}$$
$$= \text{antilog}(0.2814) = 1.91$$

or $[\text{A}]_t = 0.13$ M. Therefore, the amount of [A] decomposed $= [\text{A}]_0 - [\text{A}]_t = 0.25 - 0.13 = 0.12$ M

Thus, fraction of C formed is

$$\frac{k_1}{k_1 + k_2} \times [\text{A}](\text{decomposed}) \times \frac{1}{1} = 0.12 \times \frac{4 \times 10^{-5}}{6 \times 10^{-5}}$$
$$= 8 \times 10^{-3}\ \text{M}$$

Solved Example 12-41

A radioactive isotope A undergoes simultaneous decay to yield B and C nuclei as shown:

$$\text{A} \begin{cases} \xrightarrow{k_1} \text{B}\ (t_{1/2} = 9\ \text{h}) \\ \xrightarrow[k_2]{} \text{C}\ (t_{1/2} = 4.5\ \text{h}) \end{cases}$$

Assuming that initially neither B nor C was present, after how many hours will the amount of C be just double to the amount of A remaining?

Solution

From the given reaction, we have $t_{1/2}$ of B $= 2t_{1/2}$ of C, which means that C is formed at twice the rate of formation of B. The rate constant for the decay of A is

$$k = k_1 + k_2 = \frac{0.693}{9} + \frac{0.693}{4.5} = \frac{0.693}{3}$$

Let after time t, [C] = 2[A] and [B] = x%. Thus, the reaction can be represented as

$$\text{A}(100 - 3x) \begin{cases} \xrightarrow{k_1} \text{B}(x) \\ \xrightarrow[k_2]{} \text{C}(2x) \end{cases}$$

Thus, we have [C] = 2[A], so

$$2x = 2(100 - 3x) \Rightarrow x = 25$$

Now, for first order kinetics, we have

$$kt = \ln \frac{a}{a - x} \Rightarrow \frac{\ln 2}{3} t = \ln \frac{100}{100 - 3x} \Rightarrow 2^{t/3} = \frac{100}{25} = 4$$

Therefore, $\frac{t}{3} = 2 \Rightarrow t = 6\ \text{h}$

Reversible or Opposing Reactions

The reactions in which the products of chemical change react together to form the original reactants are called reversible reactions. These are also called opposing or counter reactions. Let us consider a reversible reaction in which both forward and backward reactions are of first order.

$$\text{A} \underset{k_\text{b}}{\overset{k_\text{f}}{\rightleftharpoons}} \text{B}$$

The differential rate law for the reaction is

$$\frac{-\text{d}[\text{A}]}{\text{d}t} = \frac{-\text{d}[\text{B}]}{\text{d}t} = k_\text{f}[\text{A}] - k_\text{b}[\text{B}] \tag{12.39}$$

If the initial concentrations of A and B are $[\text{A}]_0$ and $[\text{B}]_0$, respectively, then $[\text{A}] = [\text{A}]_0 - x$ and $[\text{B}] = [\text{B}]_0 - x$, where x is the concentration of A that has reacted to B at any time. Rewriting Eq. (12.39), we get

$$\frac{\text{d}x}{\text{d}t} = k_\text{f}([\text{A}]_0 - x) - k_\text{b}([\text{B}]_0 + x)$$

However, since $A_{eq} = [A]_0 - x_{eq}$ and $B_{eq} = [B]_0 + x_{eq}$ where A_{eq} and B_{eq} are equilibrium concentrations, we can rewrite by substituting for $[A]_0$ and $[B]_0$.

$$\frac{dx}{dt} = k_f(A_{eq} + x_{eq} - x) - k_b(B_{eq} - x_{eq} + x) = (k_f A_{eq} - k_b B_{eq}) + k_f(x_{eq} - x) + k_b(x_{eq} - x) = (k_f + k_b)(x_{eq} - x)$$

For this last equality we have used the fact that $k_f A_{eq} = k_b B_{eq}$. Rearrangement gives

$$\frac{dx}{(x_{eq} - x)} = (k_f + k_b)\,dt$$

Integrating both sides, we get
$$-\ln\frac{x_{eq} - x}{x} = (k_f + k_b)t$$

Exponentiating both sides gives
$$-\ln\frac{x_{eq} - x}{x} = (k_f + k_b)t$$

or
$$x = x_{eq}\{1 - \exp[-(k_f + k_b)t]\}$$

After subtracting both sides from $[A]_0$,
$$[A] = A_{eq} + x_{eq}\exp[-(k_f + k_b)t]$$

Thus [A] starts at $A_{eq} + x_{eq} = [A]_0$ and decreases to A_{eq} exponentially with a rate constant equal to the sum of the forward and reverse rates. Similarly, [B] starts at $B_{eq} - x_{eq} = [B]_0$ and increases to B_{eq} exponentially with the same rate constant. These relationships are shown in Fig. 12.8.

Some examples of opposing reactions are:

1. Dissociation of hydrogen iodide in gas phase: $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$
2. Reaction between CO and NO_2 gases: $CO(g) + NO_2(g) \underset{k_b}{\overset{k_f}{\rightleftharpoons}} CO_2(g) + NO_2(g)$

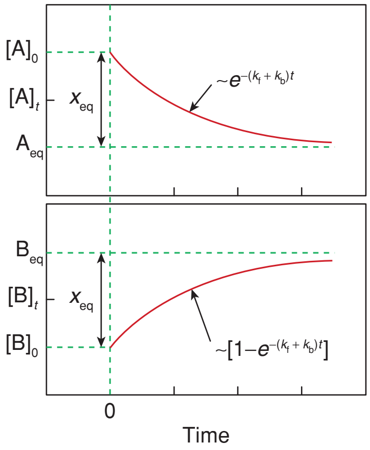


Figure 12.8 Concentrations are a function of time for opposing reactions.

Solved Example 12-42

For a reversible first order reaction, $A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} B$ where $k_f = 10^{-2}\ s^{-1}$ and $B_{eq}/A_{eq} = 4$. If $[A]_0 = 0.01$ mol L^{-1} and $[B]_0 = 0$ mol L^{-1}, what will be concentration of B after 30 s?

Solution

For the reaction $A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} B$, we have

	A ⟶	B
Initial moles	0.01	0
Moles at equilibrium	$0.01 - x_{eq}$	x_{eq}

Now, the equilibrium constant is

$$K_C = \frac{B_{eq}}{A_{eq}} = \frac{k_f}{k_b} = \frac{x_{eq}}{[A]_0 - x_{eq}}$$

Substituting given values, we get

$$4 = \frac{10^{-2}}{k_b} = \frac{x_{eq}}{0.01 - x_{eq}}$$

which gives $k_b = 2.5 \times 10^{-3}\ s^{-1}$ and $x_{eq} = 0.008$ mol L^{-1}. Now, to calculate the concentration of [B] after 30 s, we use the following expression:

$$t = \frac{2.303}{k_f + k_b}\log\frac{x_{eq}}{x_{eq} - x}$$

Given that $[B]_0 = 0$, so $[B] = [B]_0 - x = x$ mol L^{-1}. Substituting values, we get

$$30 = \frac{2.303}{1.25 \times 10^{-2}}\log\frac{0.008}{0.008 - x}$$

or
$$\frac{0.008}{0.008 - x} = \text{antilog}(0.1628) = 1.455$$

Solving, we get $x = [B] = 2.50 \times 10^{-3}$ mol L^{-1}.

12.12 | DETERMINATION OF ORDER OF SIMPLE REACTIONS – EXPERIMENTAL METHODS

For reactions involving single reactants, the order can be determined by measuring experimentally the amount of substance reacted or left at different time intervals. These values are substituted in integrated rate law equations for different orders. The equation which gives constant value of rate constant gives the order of reaction. This method is known as **integration method**. Apart from this hit and trial method, different experimental methods are used for the determination of order of a reaction and these are described as follows.

1. **Initial rate method:** This method can be used irrespective of the number of reactants involved. For example, consider the reaction

$$n_1\text{A} + n_2\text{B} + n_3\text{C} \rightarrow \text{Products}$$

The method involves finding the initial rate of reaction by taking known concentrations of the different reactants. Now, the concentrations of one of the reactants is changed (say that of A) keeping the concentrations of other reactants (B and C) same as before. The initial rate of the reaction is determined again. This gives the rate expression with respect to A and hence the order with respect to A. The experiment is repeated by changing the concentration of B and taking the same concentrations of A and C and finally changing the concentration of C and taking the same concentrations of A and B. These will give rate expressions w.r.t. B and C, and hence the orders w.r.t. B and C, respectively. Combining the different rate expressions, the overall rate expression and hence overall order can be obtained.

Suppose the order of the above reaction with respect to A, B and C are x, y and z, respectively. Then the rate is given by Rate = $k[\text{A}]^x[\text{B}]^y[\text{C}]^z$. Starting with two different initial concentrations of A, keeping the concentrations of B and C constant, the initial rates of the reaction are determined as

$$(r_0)_1 = k[\text{A}_0]_1^x[\text{B}]^y[\text{C}]^z \quad \text{and} \quad (r_0)_2 = k[\text{A}_0]_2^x[\text{B}]^y[\text{C}]^z$$

Therefore, we have

$$\frac{(r_0)_1}{(r_0)_2} = \frac{[\text{A}_0]_1^x}{[\text{A}_0]_2^x} = \left\{\frac{[\text{A}_0]_1}{[\text{A}_0]_2}\right\}^x \Rightarrow \log\frac{(r_0)_1}{(r_0)_2} = \alpha \log\frac{[\text{A}_0]_1}{[\text{A}_0]_2} \Rightarrow \alpha = \frac{\log[(r_0)_1/(r_0)_2]}{\log\{[\text{A}_0]_1/[\text{A}_0]_2\}}$$

This is the order with respect to A. Similarly, order with respect to B and C can be determined. On adding, we get the overall order of the reaction (= $x + y + z$).

2. **Graphical method:** Consider a zero order reaction of the type A → Products. Let a be the initial concentration of the reactant and x be the concentration that is consumed at time t. Then the concentration of the reactant at t is $a - x$. The rate equation is therefore,

$$\frac{\text{d}x}{\text{d}t} = k(a-x)^0 = k$$

If the reaction is of first order, the rate of reaction is given by Eq. (12.40) and if it is of second order then it is given by Eq. (12.41)

$$\frac{\text{d}x}{\text{d}t} = k(a-x) \tag{12.40}$$

$$\frac{\text{d}x}{\text{d}t} = k(a-x)^2 \tag{12.41}$$

Now, if the plot of log $(a - x)$ vs. t is a straight line, the reaction follows first order. If the plot of $1/(a - x)$. t is a straight line, the reaction follows second order. In general, for a reaction of nth order, a graph of $1/(a - x)^{n-1}$ vs. t must be a straight line.

3. **van't Hoff differential method:** We have learnt that, the rate of reaction varies as the nth power of the concentration of the reactant where n is the order of the reaction. Thus, for two different initial concentrations A_1 and A_2, equations can be written in the form

$$\frac{-dA_1}{dt} = kC_1^n \quad \text{and} \quad \frac{-dA_2}{dt} = kC_2^n$$

Taking logarithms, we get

$$\log_{10}\left(\frac{-dA_1}{dt}\right) = \log_{10} k + n\log_{10} A_1 \tag{12.42}$$

and

$$\log_{10}\left(\frac{-dA_2}{dt}\right) = \log_{10} k + n\log_{10} A_2 \tag{12.43}$$

Subtracting Eq. (12.42) from Eq. (12.43), we get

$$\log_{10}\left(\frac{-dA_1}{dt}\right) - \log_{10}\left(\frac{-dA_2}{dt}\right) = n(\log_{10} A_1 - \log_{10} A_2)$$

or

$$n = \frac{\log_{10}\left(\frac{-dA_1}{dt}\right) - \log_{10}\left(\frac{-dA_2}{dt}\right)}{(\log_{10} A_1 - \log_{10} A_2)}$$

where $-dA_1/dt$ and $-dA_2/dt$ are determined from concentration vs. time graphs and the value of n can be obtained.

4. **Half-life method:** For the same reaction, the half-lives are determined at two different concentrations and related to the order of reaction.

12.13 | EFFECT OF TEMPERATURE – ARRHENIUS THEORY

As the temperature increases, the molecules move faster and therefore collide more frequently. The molecules also have more average kinetic energy at higher temperature. The reaction rate increases by a factor of about 2 or 3 for each 10°C increase in temperature, although the actual amount of increase differs from one reaction to the other. Here, we introduce the term temperature coefficient which is defined as the ratio of rate constants measured at different temperatures T_1 and T_2 where $T_2 - T_1 = 10°\text{C}$. Mathematically, we have

$$\text{Temperature coefficient } (Q_{10}) = \frac{\text{Rate constant at } T_2}{\text{Rate constant at } T_1} = \frac{k_{T_2}}{k_{T_1}}$$

The value of temperature coefficient is nearly 2 although in some cases it approaches even 3. For example, the temperature coefficients for dissociation of HI, and for the reaction between methyl iodide and sodium ethoxide are 1.8 and 2.9, respectively.

$$2\,HI \rightarrow H_2 + I_2$$
$$CH_3I + C_2H_5ONa \rightarrow CH_3OC_2H_5 + NaI$$

Further, greater the difference in temperature, greater will be the difference in reaction rates. For example, increase of 160°C in temperature during the decomposition of acetaldehyde increases the reaction rate 453 times.

Activated Complex Theory and Concept of Activation Energy

In a given sample of gas, all the molecules do not possess similar velocity and hence kinetic energy. In fact, at a given temperature there is a definite distribution of velocities or kinetic energies amongst the various molecules of gas. At low temperature (say T_1), only a small part of the molecules has very low kinetic energy. Another small part has very high kinetic energy and a larger part has intermediate kinetic energy. Further, as the temperature is increased, from T_1 to T_2, energy re-distribution takes place. More number of molecules acquire high kinetic energy Fig. 12.9. The excess energy acquired by the real reacting molecules is known as activation energy (E_a), that is,

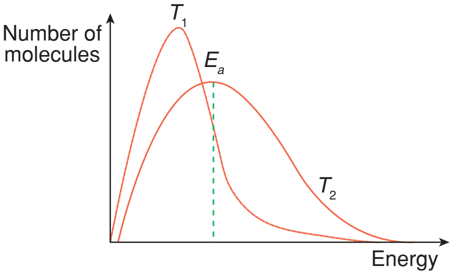


Figure 12.9 Energy distribution curve for a reaction at two different temperatures.

Activation energy = Threshold energy
– Actual energy possessed by molecules

Thus according to activation energy concept, non-active molecules (having energy less than the threshold energy) can be activated by absorption of extra energy, known as the activation energy.

According to Arrhenius theory, for a reaction to take place, the reacting molecules must collide to form an intermediate complex which is unstable and breaks up to form the products. This intermediate complex is known as the **activated complex** and the energy required to form this complex is called the **activation energy**. Consider the following reaction:

$$AC + BD \rightarrow AB + CD$$

The two reactants join to form the intermediate complex as shown in Fig. 12.10, which then dissociates to form the products.

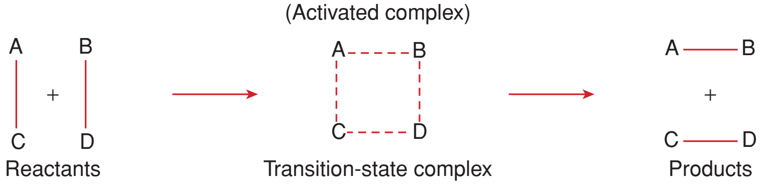


Figure 12.10 Formation of transition-state complex.

In other words, the reactant species have to acquire a certain amount of energy before they can react to yield products, that is, there is an energy barrier which must be crossed over by the reactants to be converted into the products. This energy barrier determines the magnitude of threshold energy which reactant molecules must acquire before they can yield products (Fig. 12.11).

When the energy of products is less than that of the reactants, the reaction is exothermic and thus ΔH will be negative [Fig. 12.12(a)]. The reaction is endothermic when energy of products is less than that of reactants and ΔH is positive [Fig. 12.12(b)].

Different reactions have different amount of activation energy. A reaction which has higher activation energy is slow at ordinary temperatures while the reaction, having lower activation energy will proceed at a faster rate at a given temperature. Thus the difference in activation energy is mainly responsible for observed difference in rates of reactions. From Fig. 12.12, we have the following

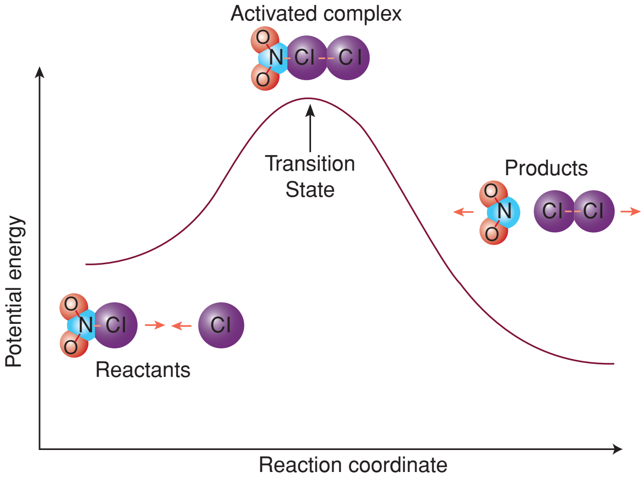


Figure 12.11 Energy barrier in chemical reactions.

1. The threshold energy $E_T = E_R + E_a$ where E_R is the energy of the reactant.
2. $E_{a(\text{forward})} = E_{a(\text{backward})} + \Delta H$

3. For exothermic reaction, $E_{a(\text{forward})} - \Delta H = E_{a(\text{backward})}$
4. For endothermic reaction, $\Delta H = E_{a(\text{forward})} - E_{a(\text{backward})}$

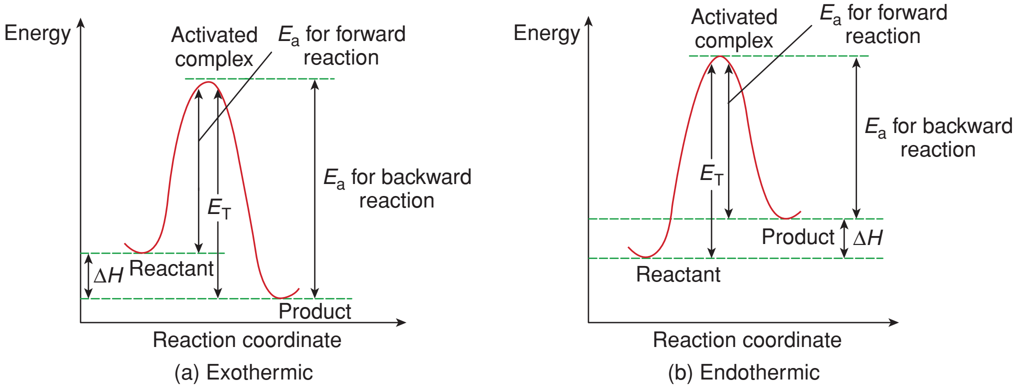


Figure 12.12 Energy profile for (a) exothermic reaction and (b) endothermic reaction

$$\frac{-d(\Delta H)}{dT} = \frac{1}{RT^2}$$

Arrhenius Equation and Calculation of Activation Energy

In 1889, Svante Arrhenius suggested that the relationship between temperature and the rate constant for a reaction obeyed the following equation:

$$k = Ae^{-E_a/RT} \tag{12.44}$$

In this equation, k is the rate constant for the reaction and A is a proportionality constant that is known as **Arrhenius factor** or **frequency factor**. It is also called pre-exponential factor and is specific for a reaction. R is the ideal gas constant in joules per mole kelvin (J mol^{-1} K^{-1}), e is the base of natural logarithms, E_a is the activation energy for the reaction and T is the temperature in kelvins. For a given A and T, the rate constant k is therefore determined by E_a.

Calculation of Activation Energy

The activation energy can be determined graphically. Equation (12.44) is normally used in its logarithmic form. If we take the natural logarithm of both sides, we obtain

$$\ln k = \ln A - \frac{E_a}{RT}$$

Let us rewrite the equation as

$$\ln k = \ln A - \left(\frac{E_a}{R}\right) \times \left(\frac{1}{T}\right) \tag{12.45}$$

We know that the rate constant k varies with the temperature T, which also means that the quantity ln k varies with the quantity ($1/T$). These two quantities, namely, ln k and $1/T$, are variables, so Eq. (12.45) is in the form of an equation for a straight line.

$$\begin{array}{ccccccc} \ln k & = & \ln A & + & (-E_a/R) & \times & (1/T) \\ \updownarrow & & \updownarrow & & \updownarrow & & \updownarrow \\ y & = & c & + & m & & x \end{array}$$

To determine the activation energy, we can make a graph of ln k vs. $1/T$. The graph is a straight line whose slope = $-E_a/R$ and intercept = ln A (Fig. 12.13).

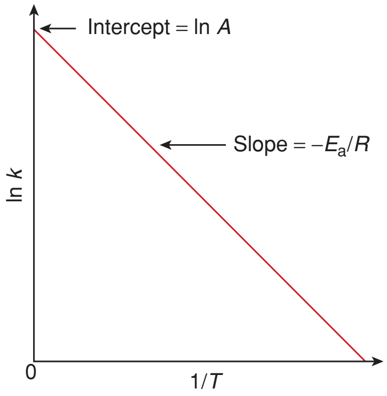


Figure 12.13 Arrhenius plot of ln k (rate constant) vs. $1/T$ (temperature).

The activation energy can be calculated from rate constants measured at two temperatures. If the activation energy and the rate constant at a particular temperature are known, the rate constant at another temperature can be calculated using a relationship, which can be derived from Eq. (12.44) as follows.

At temperature T_1, the Arrhenius equation can be written as

$$\ln k_1 = -\frac{E_a}{RT_1} + \ln A$$

Similarly at temperature T_2, the equation is $\ln k_2 = -\dfrac{E_a}{RT_2} + \ln A$

Here k_1 and k_2 are the values of rate constant at temperatures T_1 and T_2, respectively. Subtracting both the equations, we get

$$\ln k_2 - \ln k_1 = \frac{E_a}{RT_1} - \frac{E_a}{RT_2}$$

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \quad \text{or} \quad \ln \frac{k_2}{k_1} = -\frac{E_a}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

It can also be given by
$$\log \frac{k_2}{k_1} = -\frac{E_a}{2.303R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \quad \text{or} \quad \log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \tag{12.46}$$

This equation can also be used to calculate the activation energy from rate constants measured at two different temperatures.

Solved Example 12-43

A first order reaction is 50% completed in 20 min at 27°C; the same reaction is 50% complete in 5 min at 77°C. Calculate the activation energy of the reaction.

Solution

For first order reaction, half-life period is given by

$$t_{1/2} = \frac{0.693}{k} \quad \text{or} \quad k = \frac{0.693}{t_{1/2}}$$

Given that at $T_1 = 27°\text{C} = 300$ K; $t_{1/2} = 20$ min. Therefore,

$$k_1 = \frac{0.693}{20} = 0.0346\,\text{min}^{-1}$$

At $T_2 = 77°\text{C} = 305$ K; $t_{1/2} = 5$ min. Therefore,

$$k_2 = \frac{0.693}{5} = 0.1386\,\text{min}^{-1}$$

The activation energy is related to rate constants at two different temperatures by the equation

$$E_a = 2.303\,k \times \frac{T_1T_2}{T_2 - T_1} \times \log \frac{k_2}{k_1}$$

Substituting values in the equation, we get

$$E_a = 2.303 \times 8.314 \times \frac{300 \times 350}{350 - 300} \times \log \frac{0.1386}{0.0346}$$
$$= 19.147 \times 2100 \times \log 4 = 24205.63\ \text{J mol}^{-1}$$
$$= 24.205\ \text{kJ mol}^{-1}$$

Solved Example 12-44

The rate of reaction becomes three times when the temperature is changed from 298 K to 358 K. Calculate the energy of activation of reaction. Given $R = 8.314$ J $\text{K}^{-1}\text{mol}^{-1}$.

Solution

According to Arrhenius equation

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$$

Substituting the given values in the equation, we get

$$\log 3 = \frac{E_a}{2.303 \times 8.314\ \text{J K}^{-1}\ \text{mol}^{-1}}\left(\frac{358-298}{298 \times 358}\right)$$

Hence,

$$E_a = \log 3 \times 2.303 \times 8.314\ \text{J K}^{-1}\ \text{mol}^{-1} \times \frac{298 \times 358}{60}$$
$$= 16243.35\ \text{J mol}^{-1} = 16.243\ \text{kJ mol}^{-1}$$

Solved Example 12-45

The rate constant for the first order decomposition of a certain reaction is given by the equation,

$$\ln k = 14.34 - \frac{1.25 \times 10^4}{T}$$

Calculate **(a)** the energy of activation, **(b)** the rate constant at 500 K and **(c)** at what temperature will its half-life period be 256 min? **(IIT-JEE 1997)**

Solution

From the Arrhenius equation, we have

$$\log k = \log A - \frac{E_a}{2.303RT}$$

The given expression is

$$\ln k = 14.34 - \frac{1.25 \times 10^4}{T} \Rightarrow \log k = \frac{14.34}{2.303} - \frac{1.25 \times 10^4}{2.303T}$$

Comparing the two equations, we get

(a) $$\frac{E_a}{2.303R} = 1.25 \times 10^4$$

or $E_a = 1.25 \times 10^4 \times 2.303 \times 8.314 = 2.393 \times 10^5$ J

(b) When $T = 500$ K, we get

$$\ln k = 14.34 - \frac{1.25 \times 10^4}{500} = 14.34 - 25 = -10.66$$

Therefore, $k = e^{-10.66} = 2.35 \times 10^{-5}\ \text{s}^{-1}$

(c) When $t_{1/2} = 256$ min, rate constant is

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{256 \times 60} = 4.51 \times 10^{-5}\ \text{s}^{-1}$$

Substituting in the given expression, we get

$$\ln(4.51 \times 10^{-5}) = 14.34 - \frac{1.25 \times 10^4}{T}$$

or $$T = \frac{1.25 \times 10^4}{14.34 + 10.0066} = 513.4\ \text{K}$$

Solved Example 12-46

For the decomposition of dimethyl ether, A in the Arrhenius equation $k = Ae^{-E_a/RT}$ has a value of 126×10^{13} and E_a value 58.5 kcal. Calculate the half-life period for first order decomposition at 527°C.

Solution

Taking logarithm of Arrhenius equation, we get

$$\log k = \log A - \frac{E_a}{2.303RT}$$

Substituting $A = 1.26 \times 10^{13}$, $E_a = 58.5$ kcal, $T = 527 + 273 = 800$ K and $R = 1.987$ cal in the above equation, we get

$$\log k = \log(1.26 \times 10^{13}) - \frac{58.5 \times 10^2}{2.303 \times 1.987 \times 800}$$
$$= 13.1003 - 15.9799 = -2.8796$$

Therefore, we get $k = 1.32 \times 10^{-3}\ \text{s}^{-1}$ and so $t_{1/2} = 0.693\ (1.32 \times 10^{-3}) = 525$ s.

Solved Example 12-47

On the top of a certain mountain, the atmospheric pressure is 0.7 atm and pure water boils at 363 K. A climber finds that it takes 300 min to boil an egg as against 3 min at 373 K. Calculate **(a)** ratio of rate constants at 373 K and 363 K, **(b)** energy of activation for the reaction when egg boiled. Assume Arrhenius factor be same.

Solution

We know that $t \propto 1/k$, therefore,

$$3 \propto \frac{1}{k_{363}} \quad (1)$$

$$300 \propto \frac{1}{k_{373}} \quad (2)$$

Dividing Eq. (2) by Eq. (1), we get

$$\frac{k_{373}}{k_{363}} = 100$$

Now, from Arrhenius expression, we have $\log\left(\frac{k_2}{k_1}\right) = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$. Substituting values, we get

$$\log(100) = \frac{E_a}{2.303 \times 2}\left(\frac{373 - 363}{373 \times 363}\right)$$

or

$$E_a = \frac{2 \times 2.303 \times 2 \times 373 \times 363}{10}$$
$$= 124729.5588 \text{ cal} = 124.729 \text{ kcal}$$

12.14 | EFFECT OF CATALYST

A **catalyst** is a substance that changes the rate of a chemical reaction without itself being used up. In other words, all of the catalyst added at the start of a reaction is present chemically unchanged after the reaction has gone to completion. The action caused by a catalyst is called **catalysis**. The action of a catalyst can be explained on the basis of intermediate complex theory, according to which the catalyst reacts with the reactants to form a complex that is transitory in nature and breaks down to give the products; and catalyst is regenerated.

For example, aqueous solutions of hydrogen peroxide are stable until we add a small quantity of the I^- ion, a piece of platinum metal, a few drops of blood, or a freshly cut slice of turnip, at which point the hydrogen peroxide rapidly decomposes.

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

This reaction, therefore, provides the basis for understanding the effect of a catalyst on the rate of a chemical reaction.

Although the catalyst is not part of the overall reaction, it does participate in the reaction by changing the mechanism of the reaction. The catalyst provides a path to the products that has a rate-determining step with a lower activation energy than that of the uncatalyzed reaction as shown in Fig. 12.14(a). A larger proportion of the collisions that occur between reactants now have enough energy to overcome the activation energy for the reaction, as shown in Fig. 12.14(b). As a result, the rate of reaction increases. Negative catalyst or poison decreases the rate of reaction due to increase in activation energy of the reaction, as shown in Fig 12.14(c).

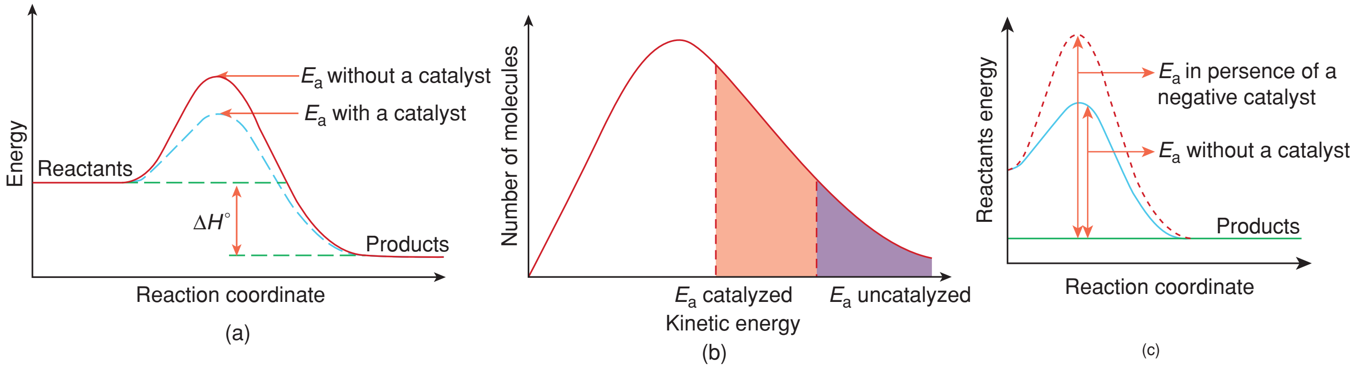


Figure 12.14 (a) A catalyst increases the rate of a reaction by providing an alternative mechanism having smaller activation energy. (b) Adding a catalyst decreases the activation energy for a reaction. (c) Effect of negative catalyst.

To illustrate how a catalyst can decrease the activation energy for a reaction by providing another pathway for the reaction, let us look again at the mechanism for the decomposition of hydrogen peroxide catalyzed by the I^- ion. In the presence of the I^- ion, the decomposition of H_2O_2 does not have to occur in a single step. It can occur in two steps, both of which are easier and, therefore, faster than the uncatalyzed reaction. In the first step, the I^- ion is oxidized by H_2O_2 to form the hypoiodite ion, OI^-.

$$H_2O_2(aq) + I^-(aq) \rightarrow H_2O(l) + OI^-(aq)$$

In the second step, the OI^- ion is reduced to I^- by H_2O_2.

$$OI^-(aq) + H_2O_2(aq) \rightarrow H_2O(l) + O_2(g) + I^-(aq)$$

Since there is no net change in the concentration of the I^- ion as a result of these reactions, the I^- ion satisfies the criteria for a catalyst. Because H_2O_2 and I^- are both involved in the first step in the reaction, and because the first step in the reaction is the rate-limiting step, the overall rate of reaction is first order in both reagents. Also, as the OI^- ion produced in the first step is consumed in the second step, it does not appear in the rate law for the reaction or as one of the products of the reaction.

The effect of several catalysts on the activation energy for the decomposition of hydrogen peroxide and the relative rate of the reaction are summarized in Table 12.3. Adding a source of I^- ion to the solution decreases the activation energy by 25%, which increases the rate of the reaction by a factor of 2000. A piece of platinum metal decreases the activation energy even further, thereby increasing the rate of reaction by a factor of 40,000. The *catalase* enzyme in blood or turnips decreases the activation energy by almost a factor of 10, which leads to a 600-billion-fold increase in the rate of reaction.

Table 12.3 Effect of catalysts on the activation energy for the decomposition of hydrogen peroxide.

Catalyst	E_a(kJ mol^{-1})	Relative rate of reaction
None	75.3	1
I^-	56.5	2.0×10^3
Pt	49.0	4.1×10^4
Catalase	8	6.3×10^{11}

Solved Example 12-48

Why is ΔH for a reaction unaffected by a catalyst?

Solution

A catalyst alters the path of the reaction but does not affect the reactants or products. Since ΔH is a state function and independent of the path of the reaction, it remains unaffected by a catalyst.

Solved Example 12-49

Assume that the activation energy was measured for both the forward (E_a = 120 kJ mol^{-1}) and reverse (E_a = 185 kJ mol^{-1}) directions of a reversible reaction. What would be the activation energy for the reverse reaction in the presence of a catalyst that decreased the activation energy for the forward reaction to 90 kJ mol^{-1}?

Solution

The activation energy of the forward reaction is reduced from 185 kJ mol^{-1} to 90 kJ mol^{-1} on addition of a catalyst. The activation energy of the forward reaction is thus lowered by $185 - 90 = 95$ kJ mol^{-1}. The activation energy of the backward reaction would also be lowered by the same amount (95 kJ mol^{-1}). Thus, the activation energy of the backward reaction in the presence of a catalyst is $120 - 95 = 25$ kJ mol^{-1}.

Solved Example 12-50

The activation energy of a non-catalyzed reaction at 37°C is 200 kcal mol^{-1} and the activation energy of the same reaction when catalyzed decreases to only 60.0 kcal mol^{-1}. Calculate the ratio of rate constants of the two reactions.

Solution

The Arrhenius equation can be written as

$$\log \frac{k_{\text{cat}}}{k_{\text{uncat}}} = \frac{1}{2.303\,RT}[E_{\text{a(uncat)}} - E_{\text{a(cat)}}]$$

Substituting given values, we get

$$\log \frac{k_{\text{cat}}}{k_{\text{uncat}}} = \frac{1}{2.303 \times 8.314 \times 310}(200 \times 10^3 - 60 \times 10^3)$$

or $$\log \frac{k_{\text{cat}}}{k_{\text{uncat}}} = 23.6 \Rightarrow \frac{k_{\text{cat}}}{k_{\text{uncat}}} = 10^{23}$$

Solved Example 12-51

A hydrogenation reaction is carried out at 500 K. If the same reaction is carried out in presence of a catalyst at the same rate, the temperature required is 400 K. Calculate the activation energy of the reaction if the catalyst lowers the activation energy barrier by 20 kJ mol^{-1}.

(IIT-JEE 2000)

Solution

Given that $k_{500} = k_{400}$, so we have

$$Ae^{-E_{a1}/RT_1} = Ae^{-E_{a2}/RT_2} \Rightarrow \frac{E_{a1}}{RT_1} = \frac{E_{a2}}{RT_2} \Rightarrow \frac{E_{a1}}{E_{a2}} = \frac{T_1}{T_2} = \frac{4}{5}$$

Given that $E_{a1} = E_{a2} + 20$ kJ. Substituting, we get

$$E_{a1} = \frac{4}{5}E_{a1} + 20 \Rightarrow E_{a1} = 100 \text{ kJ}$$

Solved Example 12-52

The energy of activation for a reaction is 100 kJ mol^{-1}. Presence of a catalyst lowers the energy of activation by 75%. What will be effect on rate of reaction at 20°C, other things being equal?

Solution

The Arrhenius equation is $k = Ae^{-E_a/RT}$. In the absence of catalyst, we have

$$k_1 = Ae^{-100/RT}$$

In presence of catalyst, we have

$$k_2 = Ae^{-25/RT}$$

So, $$\frac{k_2}{k_1} = e^{75/RT} \Rightarrow 2.303 \log \frac{k_2}{k_1} = \frac{75}{RT}$$

or $$2.303 \log \frac{k_2}{k_1} = \frac{75}{8.314 \times 10^{-3} \times 293}$$

or $$\log \frac{k_2}{k_1} = \frac{75}{8.314 \times 10^{-3} \times 293 \times 2.303}$$

or $$\frac{k_2}{k_1} = 2.34 \times 10^{13}$$

As the things being equal in presence or absence of a catalyst.

Solved Example 12-53

The rate constant is given by Arrhenius equation: $k = Ae^{-E_a/RT}$. Calculate the ratio of the catalyzed and uncatalyzed rate constant at 25°C if the energy of activation of a catalyzed reaction is 162 kJ and for the uncatalyzed reaction the value is 350 kJ.

Solution

Let k_{cat} and k_{uncat} be the rate constants for catalyzed and uncatalyzed reactions.

$$2.303 \log k_{\text{cat}} = 2.303 \log A - \frac{162 \times 10^3}{RT} \qquad (1)$$

and $$2.303 \log k_{\text{uncat}} = 2.303 \log A - \frac{350 \times 10^3}{RT} \qquad (2)$$

Subtracting Eq. (2) from Eq. (1), we get

$$\log \frac{k_{\text{cat}}}{k_{\text{uncat}}} = \frac{10^3}{2.303RT}(350 - 162)$$

$$= \frac{188 \times 10^3}{2.303 \times 8.314 \times 298} = 32.95$$

or $$\frac{k_{\text{cat}}}{k_{\text{uncat}}} = 8.88 \times 10^{32}$$

12.15 | COLLISION THEORY

Max Trautz in 1916 and William Lewis in 1918 proposed a theory known as collision theory to explain how chemical reactions occur and why at different rates. According to this theory, in a bimolecular reaction, two molecules should collide and acquire sufficient energy on collision to bring about the reaction. In fact molecules collide with each other, but all collisions are not sufficiently *effective* as few acquire activation energy.

Anything that can increase the frequency of effective collisions should, therefore, increase the rate. One of the several factors that influence the number of effective collisions per second is *concentration*. As concentration of reactant increases, the number of collisions per second of all types, including effective collisions increases. Increasing the temperature also increases the number of collisions and hence the effective number of collisions.

The number of collisions per second per unit volume of the reaction mixture is known as **collision frequency** (Z). Not every collision between reactant molecules actually results in a chemical change. We know this because the reactant atoms or molecules in a gas or in a liquid undergo an enormous number of collisions per second with each other. If every collision were effective, all reactions would be over in an instant. *But only a very small fraction of all the collisions can really lead to a net change*.

In most of the reactions, when two reactant molecules collide they must be oriented correctly for a reaction to occur. For example, let us consider the reaction discussed earlier.

$$2NO_2Cl \rightarrow 2NO_2 + Cl_2$$

Based on the equation, the reaction appears to proceed by a two-step mechanism. One step involves the collision of an NO_2Cl molecule with a chlorine atom.

$$NO_2Cl + Cl \rightarrow NO_2 + Cl_2$$

The orientation of the NO_2Cl molecule when hit by the Cl atom is important (see Fig. 12.15). The poor orientation shown in Fig. 12.15(a) cannot result in the formation of Cl_2 because the two Cl atoms are not being brought close enough together for a new Cl—Cl bond to form as an N—Cl bond breaks. Figure 12.15(b) shows the necessary orientation if the collision of NO_2Cl and Cl is to effectively lead to products.

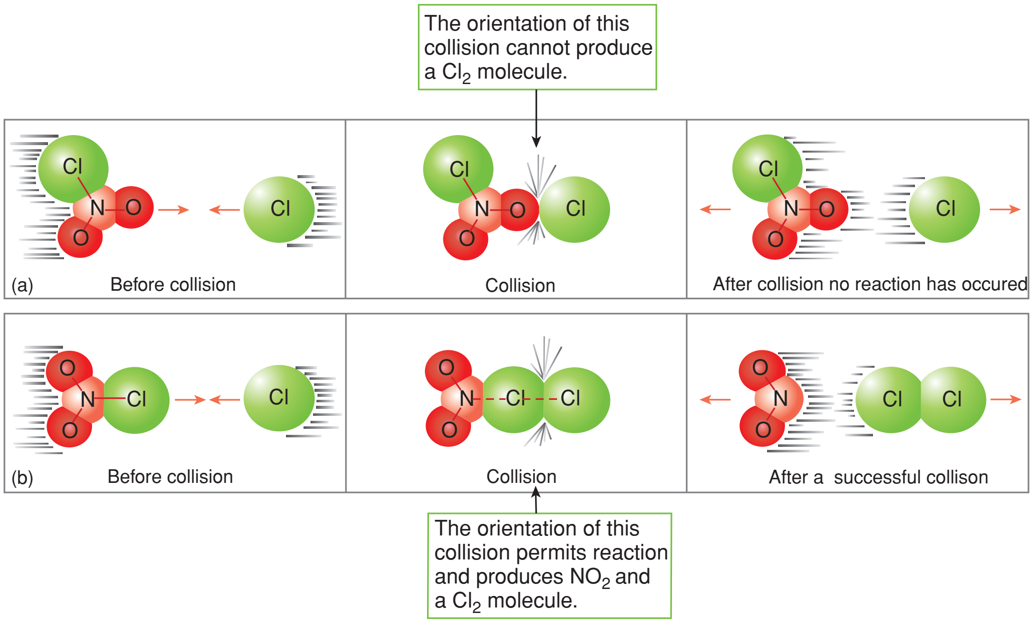

The orientation of this collision cannot produce a Cl$_2$ molecule.
Cl
N
O
O
Cl
(a)
Before collision
Collision
After collision no reaction has occured
(b)
Before collision
Collision
After a successful collison
The orientation of this collision permits reaction and produces NO$_2$ and a Cl$_2$ molecule.

Figure 12.15 Successful and unsuccessful collision between NO_2Cl molecule and Cl atom.

Note: Only about one of every billion (10^{18}) collisions leads to a net chemical reaction. In each of the other collisions the reactant molecules just bounce off each other.

In fact, molecules collide with each other, but all collisions are not sufficiently effective as only a few acquire activation energy. Thus, the rate of reaction can be related to number of collisions with proper orientation and sufficient kinetic energy. This minimum amount of kinetic energy which must be associated with molecules so that their mutual collisions to result in chemical reaction is called threshold energy.

$$\text{Activation energy} = \text{Threshold energy} - \text{Energy of colliding molecules}$$

Suppose Z is the number of molecules colliding per cm^3 per second in the reacting system containing 1 mol L^{-1} of reactant and q is the fraction of these that are activated, then reaction constant k of the reaction is given by

$$k = Zq \tag{12.47}$$

According to kinetic theory of gases, for a gas containing only one kind of molecule, the number of colliding molecules per cm^3 per second Z_1 is

$$Z_1 = \pi\sigma^2 v(n^*)^2 \tag{12.48}$$

where σ is the molecular diameter, v the average molecular velocity in cm s^{-1} and n^* the number of molecules per cm^3. When two different molecules are involved, Z is taken to be $Z_{1,2}$ and is given by

$$Z_{1,2} = n_1^* n_2^* \left[\frac{\sigma_1 + \sigma_2}{2}\right]^2 \sqrt{8\pi RT \frac{(M_2 + M_1)}{M_1 M_2}} \tag{12.49}$$

where σ_1 and σ_2 are the molecular diameters of the respective molecules, M_1 and M_2 their molecular masses, n_1^* and n_2^* the numbers of the respective molecules per cm^3 at temperature T.

From Maxwell distribution law for molecular rates, it can be deduced that, in any gas containing n^* molecules per cm^3 at a temperature T, the number of molecules, n', which will possess an energy E or higher is

$$n' = n^* e^{-E/RT} \tag{12.50}$$

If $E = E_a$, the energy of activation, the fraction of molecules activated in Eq. (12.50), can be given as

$$\frac{n'}{n^*} = e^{E_a/RT} = \frac{\text{Number of molecules activated}}{\text{Total number of molecules}}$$

And this is equal to q (fraction of these that are activated). Inserting q from Eq. (12.47), then, k becomes

$$k = Ze^{E_a/RT} \tag{12.51}$$

where Z is given by Eq. (12.48) for same type of molecules and by Eq. (12.49) for molecules of different type. Comparing with Arrhenius equation we can see that Arrhenius factor is related to collision frequency.

The calculation of k, theoretically goes along with that of experimentally determined values in several gaseous reactions and solution phase reactions. Hence the theory is considered successful. However, there are many reactions of both in gas and solution phases, where the theoretical values are too high by the factors ranging from 10^9 onwards. For such reactions, a probability factor, P is introduced to allow the disparity between calculated and observed rate constants:

$$k = PZe^{-E_a^*/RT} \tag{12.52}$$

where P may have the values ranging from unity to 10^{-9}. It is also known as the steric factor and takes into account the proper orientation of the collision.

Limitation of Collision Theory

The collision theory is applicable to simple gaseous reactions. The experimental rates of reactions between complicated molecules are found to be much smaller than the theoretically predicted rate. This discrepancy is explained by the fact that the complicated molecules are considered to be hard spheres with no internal energy. The spherical model ignores the dependence of the effectiveness of a collision on the orientation of the molecules colliding. Activation energy includes only translational motion neglecting rotational and vibrational motions. Hence this theory is applicable to reactions involving simple gas molecules.

Solved Example 12-54

What two factors influence the effectiveness of molecular collisions in producing chemical change?

Solution

The effectiveness of collisions is influenced by the orientation of the reactants and kinetic energy of the collision.

Solved Example 12-55

Which beaker has better chance of reactivity?

Beaker A: 10 mL beaker filled with 10 ml of a mixture.
Beaker B: 20 mL beaker filled with 10 ml of the same mixture.

Solution

Beaker A. This is because the concentration is increased with less space, thus giving the atoms a higher chance of having enough energy and hitting at the correct orientation.

Rising Temperature Increases Reaction Rate

The distribution of kinetic energy of the molecules may be obtained from the Maxwell–Boltzmann distribution curve which is a plot of fraction of molecules (N_E/N_T) with a given kinetic energy against the kinetic energy. Here N_E is the fraction of molecules with energy E and N_T is the total number of molecules. The peak of the curve (Fig. 12.16) corresponds to the most probable velocity and hence the **most probable kinetic energy**.

On the basis of collision theory and concept of activation energy, we can now explain why the rate of a reaction increases so much with increasing temperature. We will use the two curves in Fig. 12.17, each corresponding to a different temperature for the same mixture of reactants. Each curve is a plot of the different *fractions* of all collisions (vertical axis) that have particular values of kinetic energy of collision (horizontal axis). (The total area under a curve then represents the total number of collisions, because all of the fractions must add up to this total.) Notice what happens to the plots when the temperature is increased; the maximum point shifts to the right and the curve flattens somewhat. However, *a modest increase in temperature generally does not affect the reaction's activation energy.* Within reason, the activation energy of a reaction is not affected by a change in temperature. In other words, as the curve flattens and shifts to the right with an increase in temperature, the value of E_a stays the same.

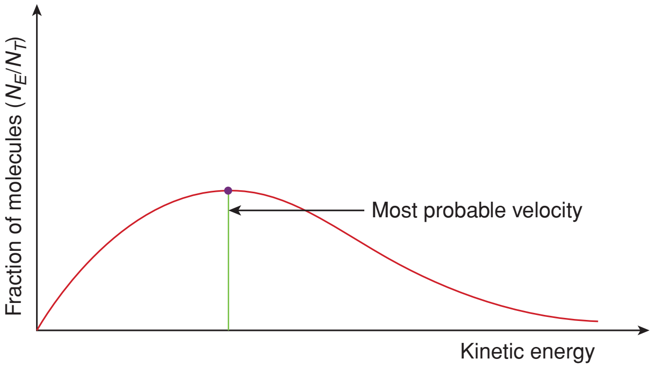
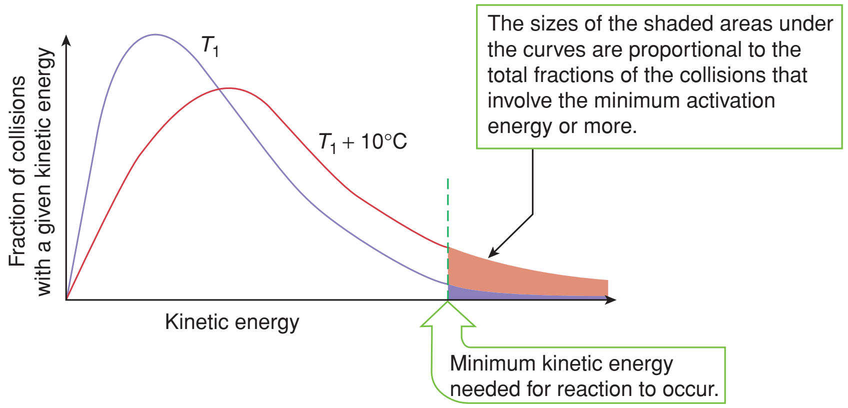


Figure 12.16 Most probable kinetic energy.



The sizes of the shaded areas under the curves are proportional to the total fractions of the collisions that involve the minimum activation energy or more.

Minimum kinetic energy needed for reaction to occur.

Figure 12.17 Kinetic energy distributions for a reaction mixture at two different temperatures.

The shaded areas under the curves in Fig. 12.17 represent the sum of all those fractions of the total collisions that equal or exceed the activation energy. This sum—we could call it the *reacting fraction*—is relatively much greater at the higher temperature than at the lower temperature because a significant fraction of the curve shifts beyond the activation energy in even a modest change to a higher temperature. In other words, at the higher temperature, a much greater fraction of the collisions occurring each second results in a chemical change, so the reactants disappear faster at the higher temperature.

SOLVED OBJECTIVE QUESTIONS FROM PREVIOUS YEAR PAPERS

1. If the concentration of a reactant decreases from 800 mol dm^{-3} to 50 mol dm^{-3} in 2×10^5 s in a first order reaction, the rate constant of the reaction would be

(A) 2×10^{-5} s
(B) 1.386×10^{-5} s
(C) 3.45×10^{-5} s
(D) 2×10^5 s

(IIT-JEE 2003)

Solution

(B) For the first order reaction, we have

$$k = \frac{2.303}{t}\log\frac{[A]_0}{[A]_t} = \frac{2.303}{2\times 10^4}\log\frac{800}{50} = 1.386 \times 10^{-5} \text{ s}$$

2. The compound A follows first order reaction: A → Products where the concentration of A, changes from 0.1 M to 0.025 M in 40 min. Find the rate of reaction of A when concentration of A is 0.01 M.

(A) 3.47×10^{-4} M min^{-1}
(B) 3.47×10^{-5} M min^{-1}
(C) 1.73×10^{-4} M min^{-1}
(D) 1.73×10^{-5} M min^{-1}

(IIT-JEE 2004)

Solution

(A) For first order reaction,

$$k = \left(\frac{2.303}{t}\right)\log\frac{[A_0]}{[A_t]} = \left(\frac{2.303}{40}\right)\log\frac{0.1\text{ M}}{0.025\text{ M}}$$

$$= \frac{2.303}{40}\log 4$$

Now, Rate = k [A], so we have

$$\text{Rate} = \frac{2.303 \times 0.6021 \times 0.01}{40} = 3.47 \times 10^{-4} \text{ M min}^{-1}$$

3. Which of the following statements is incorrect about order of a reaction?

(A) Order of a reaction can never be equal to zero or fractional value.
(B) It is always determined experimentally.
(C) It is equal to the molecularity of an elementary reaction.
(D) It is sum of the powers of concentration terms in the differential rate law of a reaction.

(IIT-JEE 2005)

Solution

(A) Equations of zero order are called zero order equations, for example, photochemical reaction between H_2 and Cl_2.

4. Consider a reaction aG + bH → Products. When concentration of both the reactants G and H is doubled, the rate increases by eight times. However, when the concentration of G is doubled keeping the concentration of H fixed, the rate is doubled. The overall order of the reaction is ________.

(A) 0
(B) 1
(C) 2
(D) 3

(IIT-JEE 2007)

Solution

(D) aG + bH → Products. The rate is directly proportional to $[G]^m\,[H]^n$
When concentration of both the reactants is doubled then,

$$\text{Rate} = [2G]^m[2H]^n = 2^m 2^n[G][H]$$

Then the rate increases eight times which means either $m = 2$ then $n = 1$ or $n = 2$ and $m = 1$. Again, it is given that when the concentration of G is doubled then rate is doubled which means that $m = 1$ and $n = 2$. And the overall order is $m + n = 2 + 1 = 3$.

5. Under the same reaction conditions, initial concentration of 1.386 mol dm^{-3} of a substance becomes half in 40 s and 20 s through first order and zero order kinetics, respectively. Ratio (k_1/k_0) of the rate constants for first order (k_1) and zero order (k_0) of the reactions is

(A) 0.5 $mol^{-1}\,dm^3$

(B) 1.0 mol dm^{-3}

(C) 1.5 mol dm^{-3}

(D) 2.0 $mol^{-1}\,dm^3$

(IIT-JEE 2008)

Solution

(A) Using half-life period method,

For first order reaction, $k_1 = 0.693/t_{1/2} = 0.693/40$

For zero order reaction $k_0 = [A]_0/2t_{1/2} = 1.386/(2 \times 20)$

Therefore,

$$\frac{k_1}{k_0} = \frac{(0.693/40)}{(40/1.386)} = 0.5\ \text{mol}^{-1}$$

6. For a first order reaction $A \rightarrow P$, the temperature (T) dependent rate constant (k) was found to follow the equation

$$\log k = -(2000)\frac{1}{T} + 6.0$$

The pre-exponential factor A and activation energy E_a, respectively, are

(A) $1.0 \times 10^6\ s^{-1}$ and 9.2 kJ mol^{-1}

(B) 6.0 s^{-1} and 16.6 kJ mol^{-1}

(C) $1.0 \times 10^6\ s^{-1}$ and 16.6 kJ mol^{-1}

(D) $1.0 \times 10^6\ s^{-1}$ and 38.3 kJ mol^{-1}

(IIT-JEE 2009)

Solution

(D) Using Arrhenius theory,

$$k = Ae^{-E_a/RT} \qquad (1)$$

It is given that

$$\log k = 6 - \frac{2000}{T} \qquad (2)$$

Also, $$\log k = \log A - \frac{E_a}{2.303RT}$$

Comparing both Eqs. (1) and (2) and solving, we get

$$6 - \frac{2000}{T} = \log A - \frac{E_a}{2.303RT}$$

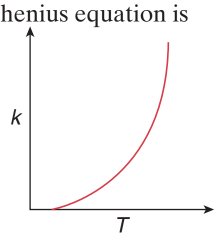
$$\log A = 6 \Rightarrow A = \text{antilog}(6) = 10^6\ s^{-1}$$

$$\frac{E_a}{2.303RT} = \frac{2000}{T}$$

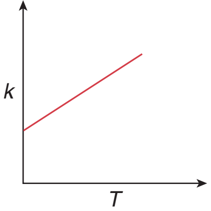
or $$E_a = 2000 \times 2.303 \times 8.31 = 38.3\ \text{kJ mol}^{-1}$$

7. Plots showing the variation of the rate constant (k) with temperature (T) are given below. The plot that follows Arrhenius equation is **(IIT-JEE 2010)**

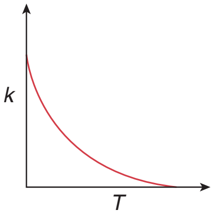
(A)



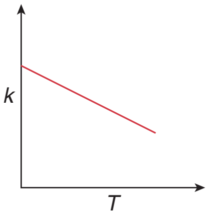
(B)



(C)



(D)



Solution

(A) According to the Arrhenius equation $k = Ae^{-E_a/RT}$. As temperature increases, rate constant (k) increases exponentially.

8. The concentration of R in the reaction $R \rightarrow P$ was measured as a function of time and the following data are obtained:

[R] (mol L^{-1})	1.0	0.75	0.40	0.10
t (min)	0.0	0.05	0.12	0.18

The order of the reaction is ________. **(IIT-JEE 2010)**

Solution

(5) From zero order kinetics, $k_1 = x/t = 0.25/0.05 = 5$ and $k_2 = x/t = 0.60/0.12 = 5$. Since the rate constants are coming to be constant, so the reaction follows zero order kinetics.

9. For the first order reaction

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

(A) The concentration of the reactant decreases exponentially with time.

(B) The half-life of the reaction decreases with increasing temperature.

(C) The half-life of the reaction depends on the initial concentration of the reactant.

(D) The reaction proceeds to 99.6% completion in eight half-life direction. **(IIT-JEE 2011)**

Solution

(A, B, D) According to first order reaction, $-d[N_2O_5]/dt = k[N_2O_5]$. The half-life can be found as

$$t = \left(\frac{2.303}{k}\right)\log\frac{a}{a-x}$$

where $a = 100$ and $a - x = 100 - 99.6 = 0.4$. The half-life period for first order reaction is

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

with temperature k increases (according to Arrhenius equation) and since $t_{1/2}$ is directly proportional to k, so if k increases then $t_{1/2}$ also increases. If the reaction completes to 99.6% completion then,

$$t_{99.6} = \left(\frac{2.303}{k}\right)\log\frac{100}{0.4} = \left(\frac{2.303}{k}\right)2.4 = 8\times\frac{0.693}{k} = 8t_{1/2}$$

10. An organic compound undergoes first order decomposition. The time taken for its decomposition to 1/8 and 1/10 of its initial concentration are $t1/8$ and $t1/10$, respectively. What is the value of $\frac{[t_{1/8}]}{[t_{1/10}]}\times 10$? (Take log 2 = 0.3.)

(IIT-JEE 2012)

Solution

(9) Using the expression for first order reaction

$$t = \frac{2.303}{k}\log\frac{[\mathrm{A}]_0}{[\mathrm{A}]_t}$$

when the compound is decomposed to 1/8th of its initial value then the time taken is

$$t_{1/8} = \left(\frac{2.303}{k}\right)\log\frac{1}{(1/8)} = \left(\frac{2.303}{k}\right)\log 8 \qquad (1)$$

when the compound is decomposed to 1/10th of its initial value then the time taken is

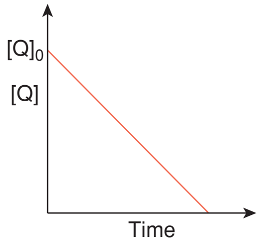
$$t_{1/10} = \left(\frac{2.303}{k}\right)\log\frac{1}{(1/10)} = \left(\frac{2.303}{k}\right)\log 10 \qquad (2)$$

Dividing Eq. (1) by Eq. (2), we get

$$\frac{t_{1/8}}{t_{1/10}} = \frac{\log 8}{\log 10} = \log(2^3) = 3\times 0.3 = 0.9$$

So, the value of $\frac{[t_{1/8}]}{[t_{1/10}]}\times 10 = 9$.

11. In the reaction, P + Q → R + S, the time taken for 75% reaction of P is twice the time taken for 50% reaction of P. The concentration of Q varies with reaction time as shown in the figure. The overall order of the reaction is



(A) 2 (B) 3 (C) 0 (D) 1 **(JEE Advanced 2013)**

Solution

(D) This is a first order reaction because $t_{75\%} = 2\times t_{50\%}$. The graph shows that the order with respect to Q is 0, so we can write the rate expression as rate = $k[\mathrm{P}]^1[\mathrm{Q}]^0$.

12. The rate law for a reaction between the substances A and B is given by Rate = $k\,[\mathrm{A}]^n\,[\mathrm{B}]^m$. On doubling the concentration of A and halving the concentration of B, the ratio of the new rate to the earlier rate of the reaction will be as

(A) $1/2^{(m+n)}$ (B) $(m+n)$
(C) $(n-m)$ (D) $2^{(n-m)}$

(AIEEE 2003)

Solution

(D) The initial and final rates are given by

$$\text{Rate}_{\text{initial}} = k[\mathrm{A}]^n[\mathrm{B}]^m \quad\text{and}\quad \text{Rate}_{\text{final}} = k[2\mathrm{A}]^n\left[\frac{1}{2\mathrm{A}}\right]^m$$

The ratio of $\text{Rate}_{\text{final}}/\text{Rate}_{\text{initial}}$ is

$$\frac{\text{Rate}_{\text{final}}}{\text{Rate}_{\text{initial}}} = \frac{k[2\mathrm{A}]^n[1/2\mathrm{A}]^m}{k[\mathrm{A}]^n[B]^m} = 2^{n-m}$$

13. For the reaction system: $2\mathrm{NO(g)} + \mathrm{O_2(g)} \rightarrow 2\mathrm{NO_2(g)}$ volume is suddenly reduced to half its value by increasing the pressure on it. If the reaction is of first order with respect to $\mathrm{O_2}$ and second order with respect to NO, the rate of reaction will be **(AIEEE 2003)**

(A) diminish to one-fourth of its initial value.
(B) diminish to one-eighth of its initial value.
(C) increase to eight times of its initial value.
(D) increase to four times of its initial value.

Solution

(C) The rate law for the reaction is Rate = $k\,[\mathrm{O_2}]\,[\mathrm{NO}]^2$. When volume is reduced to half, concentration becomes double the initial concentration, so the rate law becomes

$$\text{Rate} = k\,[2\mathrm{O_2}]\,[2\mathrm{NO}]^2 = 8k\,[\mathrm{O_2}]\,[\mathrm{NO}]^2$$

14. The half-life of a radioactive isotope is three hours. If the initial mass of the isotope were 256 g, the mass of it remaining undecayed after 18 h would be

(A) 4.0 g (B) 8.0 g
(C) 12.0 g (D) 16.0 g **(AIEEE 2003)**

Solution

(A) The amount left after n half-lives = $N_0/2^n$ where N_0 = 256 g and n = 18/3 = 6.
So, the amount left after 6 half-lives = $256/2^6 = 4.0$.

15. In respect of the equation $k = Ae^{-E_a/RT}$ in chemical kinetics, which one of the following statements is correct?

(A) k is equilibrium constant.
(B) A is adsorption factor.
(C) E_a is energy of activation.
(D) R is Rydberg's constant. **(AIEEE 2003)**

Solution

(C) E_a is the activation energy, T is the temperature, R is the gas constant and A is the pre-exponential factor.

16. In first order reaction, the concentration of the reactant decreases from 0.8 M to 0.4 M in 15 min. The time taken for the concentration to change from 0.1 M to 0.025 M is

(A) 30 min (B) 60 min
(C) 7.5 min (D) 15 min **(AIEEE 2004)**

Solution

(A) Since, the concentration of products becomes half (0.8 to 0.4 M), means $t_{1/2}$ is given as 15 min.
For a first order reaction,

$$k=\frac{0.693}{t_{1/2}}=\frac{0.693}{15}$$

Also, for a first order reaction,

$$t=\frac{2.303}{k}\log\frac{[\mathrm{A}]_0}{[\mathrm{A}]_t}=\frac{2.303}{(0.693/15)}\log\frac{0.1}{0.025}=30\text{ min}$$

17. The half-life of a radioisotope is 4 h. If the initial mass of the isotope was 200 g, the mass remaining after 24 h undecayed is

(A) 1.042 g (B) 4.167 g
(C) 3.125 g (D) 2.084 g **(AIEEE 2004)**

Solution

(C) The amount left after n half-lives $= N_0/2^n$ where $N_0 = 200$ g and $n = 24/4 = 6$.
So, the amount left after 6 half-lives = 200/26 = 3.125 g

18. The rate equation for the reaction $2\mathrm{A}+\mathrm{B}\rightarrow\mathrm{C}$ is found to be: rate $= k[\mathrm{A}][\mathrm{B}]$. The correct statement in relation to this reaction is that the

(A) unit of k must be s^{-1}.
(B) value of k is independent of the initial concentration of A and B.
(C) rate of formation of C is twice the rate of disappearance of A.
(D) $t_{1/2}$ is a constant. **(AIEEE 2004)**

Solution

(B) Value of k is independent of the initial concentration of A and B. Rate constants are independent of concentration but depend on other factors, such as temperature.

19. A reaction involving two different reactants can never be

(A) unimolecular reaction. (B) first order reaction.
(C) second order reaction. (D) bimolecular reaction.
(AIEEE 2005)

Solution

(A) This is because the minimum number of reactants is two, so the molecularity cannot be one (for molecularity = 1, there should be only one reactant).

20. The time $t_{1/4}$ can be taken as the time taken for the concentration of a reactant to drop to 3/4th of its initial value. If the rate constant for a first order reaction is k, the $t_{1/4}$ can be written as

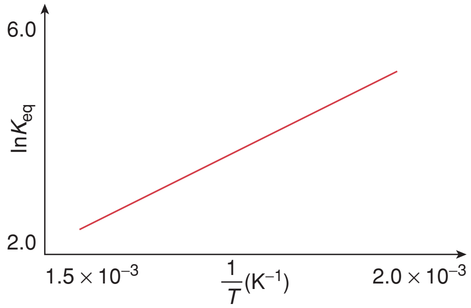
(A) $0.10/k$ (B) $0.29/k$
(C) $0.69/k$ (D) $0.75/k$ **(AIEEE 2005)**

Solution

(B) According to first order reaction,

$$t_{1/4}=\left(\frac{2.303}{k}\right)\log\left(\frac{1}{1-1/4}\right)=\frac{0.29}{k}$$

21. A schematic plot of ln K_{eq} vs. inverse of temperature for a reaction is shown below



The reaction must be
(A) exothermic.
(B) endothermic.
(C) one with negligible enthalpy change.
(D) highly spontaneous at ordinary temperature.
(AIEEE 2005)

Solution

(A) This is in accordance with Arrhenius equation $k = Ae^{-E_a/RT}$.

22. Rate of a reaction can be expressed by Arrhenius equation as: $k = Ae^{-E_a/RT}$

In this equation, E_a represents
(A) the energy above which all the colliding molecules will react.
(B) the energy below which colliding molecules will not react.
(C) the total energy of the reacting molecules at a temperature, T.
(D) the fraction of molecules with energy greater than the activation energy of the reaction. **(AIEEE 2006)**

Solution

(B) E_a is the activation energy which represents the minimum energy that the reacting molecules must possess before undergoing a reaction. As E_a increases, the rate constant k decreases.

23. The following mechanism has been proposed for the reaction of NO with $\mathrm{Br_2}$ to form NOBr:

$$\mathrm{NO(g)+Br_2(g)\rightleftharpoons NOBr_2(g)}$$

$$\mathrm{NOBr_2(g)+NO(g)\rightleftharpoons 2NOBr(g)}$$

If the second step is the rate determining step, the order of the reaction with respect to NO(g) is

(A) 1 (B) 0
(C) 3 (D) 2 **(AIEEE 2006)**

Solution

(D) From the given reactions, the rate expressions for the second reaction is

$$\text{Rate} = k[\text{NOBr}_2][\text{NO}].$$

However, $[\text{NOBr}_2] = K_C[\text{NO}][\text{Br}_2]$. Therefore,

$$\text{Rate} = k \cdot K_C\,[\text{NO}][\text{Br}_2][\text{NO}] \text{ where } K_C = \frac{[\text{NOBr}_2]}{[\text{NO}][\text{Br}_2]}$$

or $$\text{Rate} = k[\text{NO}]^2[\text{Br}_2]$$

24. A reaction was found to be second order with respect to the concentration of carbon monoxide. If the concentration of carbon monoxide is doubled, with everything else kept the same, the rate of reaction will

(A) remain unchanged
(B) triple
(C) increase by a factor of 4
(D) double **(AIEEE 2006)**

Solution

(C) For nth order reaction, the rate of reaction $\propto$ [concentration]^n
For second order reaction, the rate of reaction $\propto$ [concentration]^2. So, for the given data $\text{Rate}_1 = [\text{CO}]^2$
When concentration of CO is doubled then, $\text{Rate}_2 = [2\text{CO}]^2 = 4[\text{CO}]^2 \Rightarrow \text{Rate}_2 = 4\text{Rate}_1$.

25. Phosphorus pentachloride dissociates as follows, in a closed reaction vessel, $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$. If total pressure at equilibrium of the reaction mixture is P and degree of dissociation of PCl_5 is x, the partial pressure of PCl_3 will be under rate law

(A) $\left(\frac{x}{x+1}\right)p$
(B) $\left(\frac{2x}{1-x}\right)p$
(C) $\left(\frac{x}{x-1}\right)p$
(D) $\left(\frac{x}{1-x}\right)p$

(AIEEE 2006)

Solution

(A) The reaction can be represented as

$$\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$$

	$\text{PCl}_5(\text{g})$	$\text{PCl}_3(\text{g})$	$\text{Cl}_2(\text{g})$
Initial moles	1	0	0
Moles at equilibrium	$1-x$	x	x

The total number of moles at equilibrium
$= 1 - x + x + x = 1 + x$
Hence, the partial pressure of PCl_3 is

$$p_{(\text{PCl}_3)} = \left(\frac{x}{x+1}\right)p$$

26. The energies of activation for forward and reverse reactions for $\text{A}_2 + \text{B}_2 \rightleftharpoons 2\text{AB}$ are 180 kJ mol^{-1} and 200 kJ mol^{-1}, respectively. The presence of a catalyst lowers the activation energy of both (forward and reverse) reactions by 100 kJ mol^{-1}. The enthalpy change of the reaction ($\text{A}_2 + \text{B}_2 \rightarrow 2\text{AB}$) in the presence of catalyst will be (in kJ mol^{-1})

(A) 20
(B) 300
(C) 120
(D) 280 **(AIEEE 2007)**

Solution

(A) Consider Fig. 12.18,

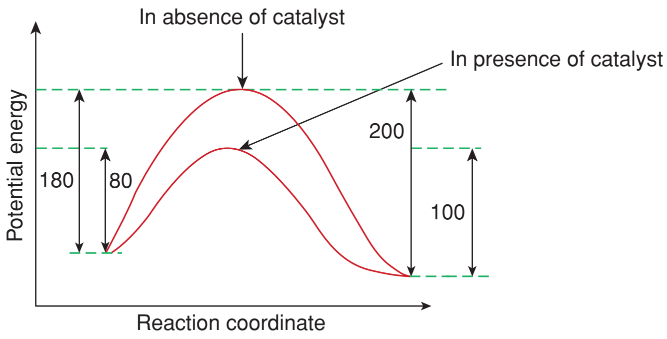


Figure 12.18

From the figure, we have

$$\Delta H(\text{reaction}) = E_{\text{af}} - E_{\text{ab}} = 80 - 100 = 20\ \text{kJ mol}^{-1}$$

27. Consider the reaction 2A + B → Products. When concentration of B alone was doubled, the half-life did not change. When the concentration of A alone was doubled, the rate increased by two times. The unit of rate constant for this reaction is

(A) s^{-1}
(B) L mol^{-1} s^{-1}
(C) no unit
(D) mol^{-1} s^{-1}

(AIEEE 2007)

Solution

(B) In the reaction 2A + B → Products, when concentration of B is doubled, the half-life did not change, hence the reaction is of first order with respect to B because half-life is independent of concentration for first order reaction ($t_{1/2} = 0.693/k$). When concentration of A is doubled, the reaction rate is doubled, hence the reaction is of first order with respect to A. So, the overall order is 1 + 1 = 2 and the units of rate constant for a second order reaction are L mol^{-1} s^{-1}.

28. A radioactive element gets spilled over the floor of a room. Its half-life period is 30 days. If the initial activity is 10 times the permissible value, after how many days will it be safe to enter the room?

(A) 100 days
(B) 1000 days
(C) 300 days
(D) 10 days **(AIEEE 2007)**

Solution

(A) We know that

$$\text{Activity}\left(-\frac{\text{d}N}{\text{d}t}\right) \propto N$$

$$N = N_0\left(\frac{1}{2}\right)^n \Rightarrow \frac{N}{N_0} = \left(\frac{1}{2}\right)^n \Rightarrow \frac{1}{10} = \left(\frac{1}{2}\right)^n \Rightarrow 10 = 2^n$$

Taking log on both the sides, $\log 10 = n \log 2$

$$n = \frac{1}{0.301} = 3.32 \text{ (as } \log 2 = 0.3010)$$

Therefore, $t = n \times t_{1/2} = 3.32 \times 30 = 99.6$ days.

29. For a reaction $\frac{1}{2}\text{A} \to 2\text{B}$, rate of disappearance of "A" is related to the rate of appearance of "B" by the expression

(A) $-\frac{d[A]}{dt} = \frac{1}{2}\frac{d[B]}{dt}$ (B) $-\frac{d[A]}{dt} = \frac{1}{4}\frac{d[B]}{dt}$

(C) $-\frac{d[A]}{dt} = \frac{d[B]}{dt}$ (D) $-\frac{d[A]}{dt} = 4\frac{d[B]}{dt}$

(AIEEE 2008)

Solution

(B) For the reaction $\frac{1}{2}\text{A} \to 2\text{B}$ for instantaneous rates,

$$\frac{dx}{dt} = \frac{-2d[A]}{dt} = +\frac{d[B]}{2dt}$$

$$\frac{dx}{dt} = \frac{-d[A]}{dt} = \frac{1}{4}\frac{d[B]}{dt}$$

30. The half-life period of a first order chemical reaction is 6.93 min. The time required for the complete 99% of the chemical reaction will be ($\log 2 = 0.301$)

(A) 46.06 min (B) 460.6 min

(C) 230.3 min (D) 23.03 min

(AIEEE 2009)

Solution

(A) Using first order reaction equation,

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{6.93} = 0.1 \text{ min}^{-1}$$

$$t = \frac{2.303}{k}\log\frac{a}{a-x}$$

where a is the initial concentration and x is the concentration at time t.

$$t = \left(2.303 \times \frac{6.93}{0.6932}\right)\log\frac{100}{1} = 46.06 \text{ min}$$

31. The time for half-life period of a certain reaction A → Products is 1 h. When the initial concentration of the reactant A is 2.0 mol L^{-1}, how much time does it take for its concentration to change from 0.50 to 0.25 mol L^{-1} if it is a zero order reaction?

(A) 1 h (B) 4 h

(C) 0.5 h (D) 0.25 h **(AIEEE 2010)**

Solution

(D) For a zero order reaction, $t_{1/2} = [\text{A}]/2k$ where [A] is the initial concentration. So, $k = [\text{A}]/2t_{1/2} = 2/2.1 = 2$. Also, for zero order reaction,

$$k = \frac{x}{t} \Rightarrow t = \frac{(0.50-0.25)}{1} = 0.25 \text{ h}$$

32. Consider the reaction:

$$\text{Cl}_2(aq) + \text{H}_2\text{S}(aq) \to \text{S}(s) + 2\text{H}^+(aq) + 2\text{Cl}^-(aq)$$

The rate equation for this reaction is rate = $k[\text{Cl}_2][\text{H}_2\text{S}]$. Which of these mechanisms is/are consistent with this rate equation?

I. $\text{Cl}_2 + \text{H}_2\text{S} \to \text{H}^+ + \text{Cl}^- + \text{Cl}^+ + \text{HS}^-$ (slow)

$\text{Cl}^+ + \text{HS}^- \to \text{H}^+ + \text{Cl}^- + \text{S}$ (fast)

II. $\text{H}_2\text{S} \rightleftharpoons \text{H}^+ + \text{HS}^-$ (fast equilibrium)

$\text{Cl}_2 + \text{HS}^- \to 2\text{Cl}^- + \text{H}^+ + \text{S}$ (slow)

(A) I only (B) II only

(C) Both I and II (D) Neither I nor II.

(AIEEE 2010)

Solution

(A) As the slowest step is the rate determining step, so from mechanism A

$$\text{Rate} = k[\text{Cl}_2][\text{H}_2\text{S}]$$

33. The rate of a chemical reaction doubles for every 10°C rise of temperature. If the temperature is raised by 50°C, the rate of the reaction increases by about **(AIEEE 2011)**

(A) 24 times. (B) 32 times.

(C) 64 times. (D) 10 times.

Solution

(B) According to Arrhenius theory, temperature coefficient $Q_{10} = 2$ (given)

$$Q_{10}^{\Delta T/10} = \frac{k_2}{k_1} \Rightarrow 2^{50/10} = 2^5 = 32 = \frac{k_1}{k_2}$$

Therefore, $32\,k_1 = k_2$. This means when the temperature is raised by 50°C, then the rate increases by 32 times.

34. For a first order reaction, A → Products, the concentration of A changes from 0.1 M to 0.025 M in 40 min. The rate of the reaction when the concentration of A is 0.01 M is

(A) 1.73×10^{-5} M min^{-1} (B) 3.47×10^{-4} M min^{-1}

(C) 3.47×10^{-5} M min^{-1} (D) 1.73×10^{-4} M min^{-1}

(AIEEE 2012)

Solution

(B) Using the expression of rate constant for first order reaction, we have

$$k = \frac{2.303}{t}\log\frac{[\text{A}]_0}{[\text{A}]_t}$$

Given that $t = 40$ min, $[\text{A}]_0 = 0.1$ M and $[\text{A}] = 0.025$ M. Therefore,

$$k = \frac{2.303}{40}\log\frac{0.1}{0.025} = 0.03465 \text{ min}^{-1}$$

Now, for first order reaction

Rate $= k[\text{A}] = 0.03465 \times 0.01 = 3.47 \times 10^{-4}$ M min^{-1}

35. The rate of a reaction doubles when its temperature changes from 300 K to 310 K. Activation energy of such a reaction will be ($R = 8.314$ JK^{-1} mol^{-1} and log 2 = 0.301)

(A) 48.6 kJ mol^{-1}
(B) 58.5 kJ mol^{-1}
(C) 60.5 kJ mol^{-1}
(D) 53.6 kJ mol^{-1}

(JEE Main 2013)

Solution

(D) As per Arrhenius equation:

$$\ln\frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$

$$2.303\log 2 = -\frac{E_a}{8.314}\left(\frac{1}{310}-\frac{1}{300}\right)$$

which gives $E_a = 53.6\,\text{kJ mol}^{-1}$.

36. For the non-stoichiometric reaction 2A + B → C + D, the following kinetic data were obtained in three separate experiments, all at 298 K.

Initial concentration (A)	Initial concentration (B)	Initial rate of formation of C (mol L^{-1} s^{-1})
0. 1 M	0.1 M	1.2×10^{-3}
0. 1 M	0.2 M	1.2×10^{-3}
0. 2 M	0.1 M	2.4×10^{-3}

The rate law for the formation of C is

(A) $\dfrac{dC}{dt} = k[A][B]$ (B) $\dfrac{dC}{dt} = k[A]^2[B]$

(C) $\dfrac{dC}{dt} = k[A][B]^2$ (D) $\dfrac{dC}{dt} = k[A]$

(JEE Main 2014)

Solution

(D) For the reaction 2A + B → C + D, the rate of formation of C is

$$\frac{d[C]}{dt} = k[A]^x[B]^y$$

From the given values in the table, we have

$$1.2\times10^{-3} = k[0.1]^x[0.1]^y \quad (1)$$

$$1.2\times10^{-3} = k[0.1]^x[0.2]^y \quad (2)$$

$$2.4\times10^{-3} = k[0.2]^x[0.1]^y \quad (3)$$

Dividing Eq. (1) by Eq. (3), we get

$$\frac{1.2\times10^{-3}}{2.4\times10^{-3}} = \frac{k[0.1]^x[0.1]^y}{k[0.2]^x[0.1]^y} \Rightarrow \frac{1}{2} = \left(\frac{1}{2}\right)^x \Rightarrow x = 1$$

Dividing Eq. (1) by Eq. (2), we get

$$\frac{1.2\times10^{-3}}{1.2\times10^{-3}} = \frac{k[0.1]^x[0.1]^y}{k[0.1]^x[0.2]^y} \Rightarrow 1 = \left(\frac{1}{2}\right)^y \Rightarrow y = 0$$

Therefore, rate of formation of C is $\dfrac{dC}{dt} = k[A]$.

37. Higher order (>3) reactions are rare due to:

(A) increase in entropy and activation energy as more molecules are involved
(B) shifting of equilibrium towards reactants due to elastic collisions
(C) loss of active species on collision
(D) low probability of simultaneous collision of all the reacting species

(JEE Main 2015)

Solution

(D) Higher order reactions are rare because the probability of collision of more than three species is very rare.

REVIEW QUESTIONS

1. In the reaction $3H_2 + N_2 \rightarrow 2NH_3$, how does the rate of disappearance of hydrogen compare to the rate of disappearance of nitrogen? How does the rate of appearance of NH_3 compare to the rate of disappearance of nitrogen?

2. For the reaction $mM \rightarrow nN$, the rate law is given by rate $= k[M]^x$. What is the significance of k and x?

3. Express the rates of following reactions in terms of disappearance of reactants and formation of products:

(a) $2NO(g) + O_2(g) \rightarrow 2NO(g)$

(b) $H_2(g) + I_2(g) \rightarrow 2HI(g)$

4. Write Arrhenius equation and explain the significance of all terms in it.

5. What are the important features of collision theory?

6. Explain why a second order reaction behaves as a first order reaction when one of the reactants is present in large excess.

7. The boiling point of water depends on atmospheric pressure. As a result, water boils at a lower temperature at 3048 m in the mountains than at sea level. Use the Arrhenius equation to describe why it takes longer to cook a hard-boiled egg at the top of a mountain than it does at sea level.

8. Why is collision theory applicable to simple gaseous molecular reaction?

9. Why is the potential energy of the molecules shown lowered in the energy profile diagram of reactants and products?

10. Differentiate between consecutive, reversible and parallel reactions by giving examples.

11. Explain the following terms: **(a)** activated complex; **(b)** temperature coefficient of a reaction.

12. When there are only trace quantities of NO in the atmosphere, it does not react with O_2 to form NO_2. As the concentration of NO in the atmosphere builds up, however, it reaches a point at which this reaction can and does occur.

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

The experimentally determined rate law for the reaction is

$$\text{Rate} = k[NO]^2[O_2]$$

Classify the order of this reaction.

13. For a second order reaction with two different reactants, half life period cannot be determined. Why?

14. According to the Arrhenius relationship between E_a and k, is k large or small when E_a is large? What does a small k mean concerning how fast the reaction proceeds? Use this relationship to suggest how catalysts speed up reactions.

15. Consider a reaction that was carried out twice, once with an initial concentration of 1 M and then with an initial concentration of 2 M. How will the half-life for the second trial compare to the half life of the first trial for zero order and first order reactions?

16. **(a)** Draw the potential energy diagram for an endothermic reaction. Indicate on the diagram the activation energy for both the forward and reverse reactions. Also indicate the heat of reaction.

(b) Explain, in terms of the law of conservation of energy, why an endothermic reaction leads to a cooling of the reaction mixture (provided heat cannot enter from outside the system).

17. Suppose a reaction occurs with the mechanism

(I) $2A \rightleftharpoons A_2$ (fast)
(II) $A_2 + E \rightarrow B + C$ (slow)

In which the first step is a very rapid reversible reaction that can be considered to be essentially an equilibrium (forward and reverse reactions occurring at the same rate) and the second is a slow step.

(a) Write the rate law for the forward reaction in step (I).
(b) Write the rate law for the reverse reaction in step (II).
(c) Write the rate law for the rate-determining step.
(d) What is the chemical equation for the net reaction that occurs in this chemical change?
(e) Use the results of parts (a) and (b) to rewrite the rate law of the rate-determining step in terms of the concentrations of the reactants in the overall balanced equation for the reaction.

18. Explain how a small rise in temperature appreciably increases the rate of reaction.

NUMERICAL PROBLEMS

1. In an experiment, the concentration of a reactant was tripled. The rate increased by a factor of 27. What is the order of the reaction with respect to the reactant?

2. The following data were collected for the reaction M + N → P + Q.

Initial concentrations (mol L^{-1})		Initial rate of reaction (mol $L^{-1}s^{-1}$)
[M]	[N]	
0.010	0.010	2.5×10^{-3}
0.020	0.010	5.0×10^{-3}
0.020	0.030	4.5×10^{-2}

Use data to obtain the rate law and the rate constant for the reaction.

3. The reaction of sucrose with water was found to be first order with respect to sucrose. The rate constant under the conditions of the experiments was 6.17×10^{-4} s^{-1}. Calculate the value of $t_{1/2}$ for this reaction in minutes. How many minutes would it take for three-quarters of the sucrose to react?

4. The ^{14}C content of an ancient piece of wood was found to be one-eighth of that in living trees. How many years old is this piece of wood ($t_{1/2}$ = 5730 years for ^{14}C)? (Hint: Recall the relationship between the integrated rate equation and half-life.)

5. The rate law for the reaction Ester + H^+ → Acid + Alcohol, is $\frac{dx}{dt} = k[\text{ester}]$. What would be the effect on rate if **(a)** concentration of ester is doubled and **(b)** concentration of H^+ ion is doubled?

6. For the reaction A → B, the rate law expression is $-\frac{d[A]}{dt} = k[A]^{1/2}$. If initial concentration of A is $[A]_0$, calculate **(a)** integrated form of the rate expression, **(b)** nature of plot of $[A]^{1/2}$ versus time and **(c)** half-life period.

7. For a homogeneous gaseous phase reaction: 2A → 3B + C, the initial pressure of reactant was p^o while pressure at time t was p. Find the pressure after time $2t$. Assume first order reaction.

8. The vapor phase decomposition of ethylene oxide into methane and CO at 414.5°C. Calculate k for first order reaction:

Time (min)	0	5	7	12	18
Pressure (mm Hg)	116.51	122.72	125.72	133.23	141.37

9. Decomposition of diazobenzene chloride was followed at constant temperature by measuring volume of N_2 evolved at definite intervals of time. Calculate order and rate constant.

Time (min)	0	2.0	5.5	7.0	∞
Volume of N_2 (mL)	0	10	25	35	163

10. A freshly cut piece of wood gives 16100 counts of β-ray emission per minute per kg and an old wooden bowl gives 13200 counts per minute per kg. Calculate the age of the wooden bowl. The half-life period of ^{14}C is 5568 years.

11. Two reactions of same order have equal exponential factors but their activation energy differ by 24.9 kJ mol^{-1}. Calculate the ratio between the rate constants of these reactions at 27°C. ($R = 8.314$ J K^{-1} mol^{-1})

12. In a second order reaction, where the initial concentration of the reactants is the same, half of the reactants are consumed in 30 min. If the rate constant is 3.6×10^{-2} L mol^{-1} min^{-1}, what is the initial concentration of the reactants?

13. For the reaction, $A(g) \rightarrow 2B(g) + C(g)$

Pressure of A at $t = 0$ is 380 mm Hg and pressure of A after 30 s is 190 mm Hg. Calculate total pressure in mm of Hg after 60 s.

14. In a reaction, $aA \rightarrow$ products, the rate is doubled when the concentration of A is increased 4 times. If 50% of the reaction occurs in 1414s, how many seconds would it take for the completion of 75% reaction ?

15. ^{64}Cu (half-life = 12.8 h) decays by β^- emission (38%), β^+ emission (19%) and electron capture (43%). Write the decay products and calculate partial half-lives for each of the decay processes

16. In a second order reaction, the initial concentration of the reactant is 0.2 mol L^{-1}. The reaction was 40% complete in 20 min. Calculate **(a)** rate constant, **(b)** time required for 75% completion of reaction and **(c)** half-life period.

17. Arsine decomposes on heating to give As and H_2. The decomposition studied at constant volume and temperature gives the following data. Calculate velocity constant, assuming first order reaction.

Time (h)	0	5.5	6.5	8
Pressure (atm)	0.9654	1.06	1.1	1.076

18. According to the reaction

$$Cr_2O_7^{2-} + 5H^+ + 3HNO_2 \rightarrow 2Cr^{3+} + 3NO_3^- + 4H_2O$$

The rate of disappearance of $Cr_2O_7^{2-}$ is found to be 2.4×10^{-4} mol L^{-1} s^{-1}. Find the rate of appearance of Cr^{3+} during given time interval.

19. The half-life of Pb^{12} is 10.6 h. It undergoes decay to its daughter (unstable) element ^{212}Bi of half-life 60.5 min. Calculate the time at which daughter element will have maximum activity.

20. Ten gram atoms of an α-active radio isotope are disintegrating in a sealed container. In one hour the helium gas collected at STP is 11.2 cm^3. Calculate the half-life of the radio-isotope.

21. At 155°C the gas phase decomposition of di-t-butyl peroxide is a first order reaction.

$$(CH_3)_3COOC(CH_3)_3 \rightarrow 2CH_3CH_3 + C_2H_6$$

The following data were obtained during experiments. Calculate rate constant for the reaction.

Time (min)	0	12	21
Total pressure (mm Hg)	170	240	280

22. A wooden door lintel from an excavated site would be expected to have what ratio of carbon-14 to carbon-12 atoms if the lintel is 9.0×10^3 years old?

23. Cooking an egg involves the denaturation of a protein called albumen. The time required to achieve a particular degree of denaturation is inversely proportional to the rate constant for the process. This reaction has a high activation energy, $E_a = 418$ kJ mol^{-1}. Calculate how long it would take to cook a traditional three-minute egg on top of mountain peak on a day when the atmospheric pressure there is 355 mm Hg.

24. The rate of reaction is doubled when the temperature is changed from 298 K to 308 K. Calculate the energy of activation of the reaction.

ADDITIONAL OBJECTIVE QUESTIONS

Single Correct Choice Type

1. For the chemical reaction $X \rightarrow Y$, it is found that the rate of reaction increases by 2.25 times when the concentration of X is increased by 1.5 times, what is the order with respect to X?
(A) zero (B) one
(C) two (D) three

2. A particular reaction increases by a factor of 2 when the temperature is increased from 27°C to 31°C. Hence activation energy of the reaction is
(A) 12.9 kcal mol^{-1} (B) 0.14 kcal mol^{-1}
(C) 1.1 kcal mol^{-1} (D) None of these

3. For a first order reaction, the units of Arrhenius factor (A) will be
(A) J K^{-1} s^{-1} (B) s^{-1}
(C) mol L^{-1} s^{-1} (D) J K^{-1} L^{-1} s^{-1}

4. For an elementary reaction $2\text{A} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{B}$. the rate of disappearance of A is equal to:

(A) $\frac{2k_1}{k_2}[\text{A}]^2$
(B) $-2k_1[\text{A}]^2 + 2k_2[\text{B}]$
(C) $2k_1[\text{A}]^2 - 2k_2[\text{B}]$
(D) $(2k_1 - k_2)[\text{A}]$

5. The rate of the gaseous reaction: $\text{A(g)} + \text{B(g)} \rightarrow$ Product is given by expression

$$-\frac{\text{d}x}{\text{d}t} = k[\text{A}][\text{B}]$$

If the volume of the reaction vessel is suddenly reduced to one fourth of the initial volume, the ratio of final rate to initial rate is:

(A) 4:1
(B) 2:1
(C) 16:1
(D) 1:2

6. For the reaction, 3A → 2B, rate of reaction $\frac{+\text{d[B]}}{\text{d}t}$ is equal to:

(A) $-\frac{3}{2}\frac{\text{d[A]}}{\text{d}t}$
(B) $-\frac{2}{3}\frac{\text{d[A]}}{\text{d}t}$
(C) $-\frac{1}{3}\frac{\text{d[A]}}{\text{d}t}$
(D) $+2\frac{\text{d[A]}}{\text{d}t}$

7. The inversion of cane sugar is represented by $\text{C}_{12}\text{H}_{22}\text{O}_{11} + \text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + \text{C}_6\text{H}_{12}\text{O}_6$. It is a reaction that is

(A) second order.
(B) pseudounimolecular.
(C) unimolecular.
(D) none of these.

8. For the reaction $\text{H}_2\text{(g)} + \text{I}_2\text{(g)} \rightarrow 2\text{HI(g)}$, the rate of disappearance of H_2 is 1.0×10^{-4} mol L^{-1} s^{-1}. The rate of appearance of HI will be

(A) 1.0×10^{-4} mol L^{-1} s^{-1}
(B) 0.50×10^{-4} mol L^{-1} s^{-1}
(C) 2.0×10^{-4} mol L^{-1} s^{-1}
(D) 4.0×10^{-4} mol L^{-1} s^{-1}

9. The units of rate constant and rate of a reaction are identical for

(A) zero order reaction.
(B) first order reaction.
(C) second order reaction.
(D) third order reaction.

10. The chemical reaction $2\text{O}_3\text{(g)} \rightarrow 3\text{O}_2\text{(g)}$ proceeds as follows.

$$\text{O}_3 \rightleftharpoons \text{O}_2 + \text{O(fast)} : \text{O}_3 + \text{O} \rightarrow 2\text{O}_2\text{(slow)}$$

The rate law expression is

(A) rate $= k[\text{O}_3]^2$
(B) rate $= k[\text{O}_3]^2[\text{O}_2]^-$
(C) rate $= k[\text{O}_3][\text{O}_2]$
(D) None of these

11. For a first order reaction,

(A) $t_{0.75} = 3t_{0.5}$
(B) $t_{0.75} = 2t_{0.5}$
(C) $t_{0.75} = 1.5t_{0.5}$
(D) $t_{0.75} = 4t_{0.5}$

12. Graph between log k and $(1/T)$ is linear of slope S (magnitude) Hence E_a is

(A) $R \times S$
(B) S/R
(C) R/S
(D) 2.303 RS

13. Reaction rates are determined by all of the following factors except

(A) the number of collisions between molecules.
(B) the force of collisions between molecules.
(C) the orientation of collisions between molecules.
(D) the spontaneity of the reaction.

14. For the reaction A + 2B → C, rate is given by Rate $= [\text{A}][\text{B}]^2$, then the order of the reaction is :

(A) 3
(B) 6
(C) 5
(D) 7

15. For the reaction $\text{H}_2\text{(g)} + \text{Br}_2\text{(g)} \rightarrow 2\text{HBr(g)}$, the experimental data suggests Rate $= k[\text{H}_2][\text{Br}_2]^{1/2}$. The molecularity and order of reaction for the reaction is, respectively,

(A) 2 and 2
(B) 2 and 3/2
(C) 3/2 and 2
(D) 3/2 and 3/2

16. If the rate of the reaction is equal to the rate constant, the order of the reaction is

(A) 1
(B) 2
(C) 3
(D) 0

17. The one which is unimolecular reaction is

(A) $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$
(B) $\text{N}_2\text{O}_5 \rightarrow \text{N}_2\text{O}_4 + \frac{1}{2}\text{O}_2$
(C) $\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl}$
(D) $\text{PCl}_3 + \text{Cl}_2 \rightarrow \text{PCl}_5$

18. The half-life of a first order reaction is 10 min. If initial amount is 0.08 mol L^{-1} and concentration at some instant is 0.01 mol L^{-1}, then t is

(A) 10 min.
(B) 30 min.
(C) 20 min.
(D) 40 min.

19. k for a zero order reaction is 2×10^{-2} mol L^{-1} s^{-1}. If the concentration of the reactant after 25 s in 0.5 M, the initial concentration must have been

(A) 0.5 M
(B) 1.25 M
(C) 12.5 M
(D) 1.0 M

20. Velocity constant of a reaction at 290 K was found to be 3.2×10^{-3}. At 300 K, it will be

(A) 1.28×10^{-2}
(B) 9.6×10^{-3}
(C) 6.4×10^{-3}
(D) 3.2×10^{-4}

21. In the titration between oxalic acid and acidified potassium permanganate, the manganous salt formed catalyzes the reaction. The manganous salt is

(A) a promoter.
(B) a positive catalyst.
(C) an autocatalyst.
(D) none of these.

22. The temperature coefficient of two reactions are 2 and 3 respectively. Which would be correct for these reactions?

(A) $E_{\text{a}1} < E_{\text{a}2}$
(B) $E_{\text{a}1} > E_{\text{a}2}$
(C) $E_{\text{a}1} = E_{\text{a}2}$
(D) Cannot be predicted.

23. The formation of gas at the surface tungsten due to adsorption is the reaction of order

(A) 0
(B) 1
(C) 2
(D) Insufficient data

24. The rate of a gaseous reaction is given by the expression k [A] [B], if the volume of the reaction vessel is suddenly reduced to 1/4th of the initial volume, the reaction rate relating to original rate will be

(A) 1/10
(B) 1/8
(C) 8
(D) 16

25. For a reaction: 2A + B → Products, the active mass of B is kept constant and that of A is doubled. The rate of reaction will then

(A) increase two times.
(B) increase four times.
(C) decrease two times.
(D) decrease four times.

26. Diazonium salt decomposes as $\text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^- \rightarrow \text{C}_6\text{H}_5\text{Cl} + \text{N}_2$. At 0°C, the evolution of N_2 becomes two

times faster when the initial concentration of the salt is doubled. Therefore, it is
(A) a first order reaction.
(B) a second order reaction.
(C) independent of the initial concentration of the salt.
(D) a zero order reaction.

27. Units of rate constant of first and zero order reactions in terms of molarity *M* unit are, respectively,
(A) s^{-1}, $M\ s^{-1}$
(B) $s^{-1}\ M$
(C) $M\ s^{-1}$, s^{-1}
(D) M, s^{-1}

28. The rate of reaction is doubled for every 10° rise in temperature. The increase in reaction rate as a result of temperature rise from 10° to 100° is
(A) 112
(B) 512
(C) 400
(D) 614

29. An example of autocatalytic reaction is
(A) The decomposition of nitroglycerine.
(B) Thermal decomposition of $KClO_3$ and MnO_2 mixture.
(C) Break down of $^{14}_{6}C$.
(D) Hydrogenation of vegetable oil using nickel catalyst.

30. It takes 10 min for the decomposition of 50% H_2O_2. If the reaction is of first order, the rate constant will be
(A) 0.693
(B) 0.00693
(C) 0.0693
(D) 6.93

31. Two substances A and B are present such that $[A]_0 = 4[B_0]$ and half-life of A is 5 min and that of B is 15 min. If they start decaying at the same time following first order kinetics, how much time later will the concentration of both of them would be same?
(A) 15 min
(B) 10 min
(C) 5 min
(D) 12 min

32. H_2O and oxygen atoms react in upper atmospheric level bimolecularly to form two OH radicals having heat of reaction 72 kJ at 400 K and energy of activation being 77 kJ mol^{-1}. E_a for bimolecular combination of two OH radicals to form H_2O and O atom is
(A) −5kJ
(B) +5 kJ
(C) −10 kJ
(D) +10 kJ

33. The mechanism of the reaction: $Nu^- + R\text{–}X \rightarrow R\text{–}Nu + X^-$ is
$Nu^- + R\text{–}X \rightarrow$ [Transition state] (slow)
[Transition state] $\rightarrow Nu\text{–}R + X^-$ (fast)

The rate of reaction can be increased by:
(A) increasing the concentration of Nu^- only.
(B) increasing the concentration of R–X only.
(C) Increasing the concentrations of both Nu^- and R–X.
(D) decreasing the concentrations of both Nu^- and R–X.

34. At the intersection point of two curves $nA \rightarrow mB$ shown in Fig. 12.19, the concentration of B can be given by

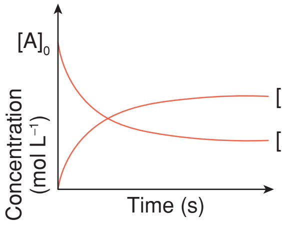


Figure 12.19

(A) $\frac{m}{m+n}[A]_0$
(B) $\frac{m}{n}[A]_0$
(C) $\frac{m}{m-n}[A]_0$
(D) $\frac{n}{m+n}[A]_0$

35. Reaction $A + 2B + C \rightarrow$ Product, follows the rate law:

$$-\frac{d[C]}{dt} = k[A]^2$$

The false statement regarding the above reaction is:
(A) On doubling the concentrations of B and C the rate of the reaction remains unaffected.
(B) On reducing the concentration of A to half, the rate becomes one-fourth.
(C) Half-life period of the reaction depends upon the concentration of B.
(D) Half-life period of the reaction is inversely proportional to the first power concentration of A.

36. The $t_{1/2}$ of first order reaction is 10 min. Starting with 100 g^{-1} of the reactant, the amount remaining after one hour is
(A) 25.0 g
(B) 3.130 g
(C) 12.50 g
(D) 1.563 g

37. The rate of the reaction: $A + B + C \rightarrow$ Products is given by

$$\text{Rate} = \frac{d[A]}{dt} = k[A]^{1/2}[B]^{1/4}[C]^0$$

The order of reaction is
(A) 1/2
(B) 4
(C) 3/4
(D) 3/2

38. If 8.0 g of a radioactive isotope has a half-life period of 10 h. The half-life period of 2.0 g of the same substance is
(A) 2.5 h
(B) 5.0 h
(C) 10 h
(D) 40 h

39. For the reaction, $2NO \rightarrow N_2 + O_2$, the expression $-\frac{1}{2}\frac{d[NO]}{dt}$ represents
(A) The rate of formation of NO.
(B) The average rate of the reaction.
(C) The instantaneous rate of reaction.
(D) All of these.

40. For the system $A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$, $\Delta H = -160$ kJ. If the activation energy for the forward step is 100 kcal mol^{-1}, what is the ratio of temperature at which the forward and backward reactions show the same percentage change of rate constant per degree rise of temperature? (1 cal = 4.2 J)
(A) $\sqrt{0.72}$
(B) $\sqrt{0.84}$
(C) $\sqrt{0.42}$
(D) $\sqrt{1}$

41. For the reaction $R-X + OH^- \rightarrow ROH + X^-$. The rate is given as

$$\text{Rate} = 5.1 \times 10^{-5}\,[R\text{–}X]\,[OH^-] + 0.20 \times 10^{-5}[R\text{–}X]$$

What percentage of R–X reacted by S_N2 mechanism when $[OH^-] = 10^{-2}$ M?
(A) 96%
(B) 3.9%
(C) 80%
(D) 20%

42. The plot of log k versus $1/T$ is linear with a slope of

(A) $\dfrac{E_a}{R}$ (B) $\dfrac{-E_a}{R}$

(C) $\dfrac{E_a}{2.303R}$ (D) $\dfrac{-E_a}{2.303R}$

43. The high temperature (≈1200 K) decomposition of $CH_3COOH(g)$ occurs as follows as per simultaneous first order reactions.

$$CH_3COOH \xrightarrow{k_1} CH_4 + CO_2$$
$$CH_3COOH \xrightarrow{k_2} CH_2CO + H_2O$$

What would be the % of CH_4 by mole in the product mixture (excluding CH_3COOH)?

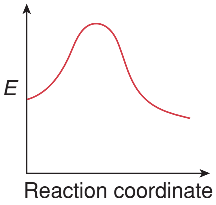
(A) $\dfrac{50k_1}{(k_1+k_2)}$ (B) $\dfrac{100k_1}{(k_1+k_2)}$

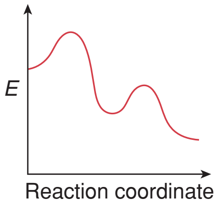
(C) $\dfrac{200k_1}{(k_1+k_2)}$ (D) It depends on time.

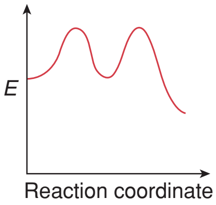
44. The solvolysis of 2-chloro-2-methyl propane in aqueous acetone:

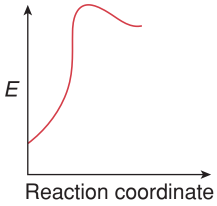
$$H_2O + (CH_3)_3C\text{–}Cl \rightarrow HO\text{–}C(CH_3)_3 + H^+Cl^-$$

has a rate equation Rate $= k[(CH_3)_3C\text{–}Cl]$. From this it may be inferred that the energy profile of the reaction leading from reactants to products is

(A) 

(B) 

(C) 

(D) 

45. The reaction $A(g) + 2B(g) \rightarrow C(g) \rightarrow D(g)$ is an elementary process. In an experiment, the initial partial pressure of A and B are $p_A = 0.60$ and $p_B = 0.80$ atm. When $p_C = 0.2$ atm, the rate of reaction relative to the initial rate is

(A) 1/48 (B) 1/24

(C) 9/16 (D) 1/6

46. A zero order reaction is one

(A) in which reactants do not react.

(B) in which one of the reactants is in large excess.

(C) whose rate does not change with time.

(D) whose rate increases with time.

47. Following reaction was carried out at 300 K.

$$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$$

How is the rate of formation of SO_3 related to the rate of disappearance of O_2?

(A) $-\dfrac{\Delta[O_2]}{\Delta t} = +\dfrac{1}{2}\dfrac{\Delta[SO_3]}{\Delta t}$ (B) $-\dfrac{\Delta[O_2]}{\Delta t} = \dfrac{\Delta[SO_3]}{\Delta t}$

(C) $-\dfrac{\Delta[O_2]}{\Delta t} = -\dfrac{1}{2}\dfrac{\Delta[SO_3]}{\Delta t}$ (D) None of these

48. According to collision theory of reaction

(A) every collision between reactant molecules leads to a chemical reaction.

(B) rate of reaction is proportional to the velocity of the molecules.

(C) rate of reaction is proportional to the average energy of the molecules.

(D) rate of reaction is proportional to the number of collision per second.

49. The integrated rate equation is $Rt = \log C_0 - \log C_t$. The straight line graph is obtained by plotting

(A) time vs. $\log C_t$ (B) $\dfrac{1}{\text{time}}$ vs. C_t

(C) time vs. C_t (D) $\dfrac{1}{\text{time}}$ vs. $\dfrac{1}{C_t}$

50. The decomposition of A into product has value of k as $4.5 \times 10^3\ s^{-1}$ at 10°C and energy of activation 60 kJ mol^{-1}. At what temperature, would k be $1.5 \times 10^4\ s^{-1}$?

(A) 12°C (B) 24°C

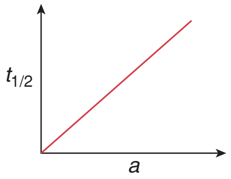
(C) 48°C (D) 36°C

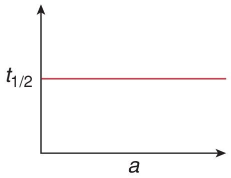
51. If concentrations are measured in mol L^{-1} and time in min, the unit for the rate constant of a third order reaction is

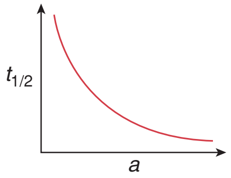
(A) mol L^{-1} min^{-1} (B) L^2 mol^{-2} min^{-1}

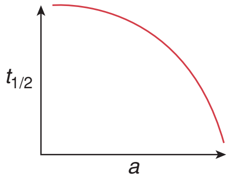
(C) L mol^{-1} min^{-1} (D) min^{-1}

52. Which of the following curves represents a first order reaction?

(A) 

(B) 

(C) 

(D) 

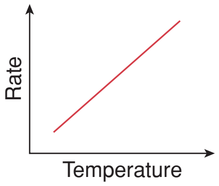
53. Calculate the order of the reaction in A and B.

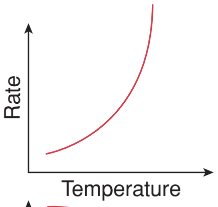
[A] (mol L^{-1})	0.05	0.10	0.05
[B] (mol L^{-1})	0.01	0.05	0.10
Rate (mol L^{-1} s^{-1})	1.2×10^{-3}	2.4×10^{-3}	1.2×10^{-3}

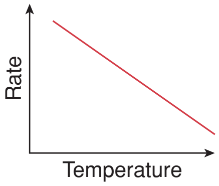
(A) 1 and 0 (B) 1 and 1

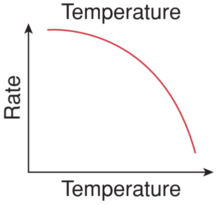
(C) 0 and 1 (D) None of these

54. Which of the following correctly represents the variation of the rate of the reaction with temperature?

(A)


(B)


(C)


(D)


55. Consider the following reactions:

(I) $H_2 + Cl_2 \xrightarrow{\text{Sunlight}} 2HCl$ (II) $H_2 + Br_2 \rightarrow 2HBr$

(III) $H_2 + I_2 \rightarrow 2HI$

The order of the reactions is

(A) 2, 1, 0
(B) 0, 3/2, 2
(C) 1, 2, 2
(D) 2, 1, 1

56. If a reaction A + B → C is exothermic to the extent of 30 kJ mol^{-1} and the forward reaction has an activation energy 70 kJ mol^{-1}, the activation energy in kJ mol^{-1} for the reverse reaction is

(A) 30
(B) 40
(C) 70
(D) 100

57. The rate of a gaseous reaction is generally expressed in terms of dp/dt. If it were expressed in terms of change in number of moles per unit time (dn/dt) or in terms of change in molar concentration per unit time (dC/dt), which of the following relationship will hold good?

(A) $\dfrac{dC}{dt} = \dfrac{dn}{dt} = \dfrac{dp}{dt}$

(B) $\dfrac{dC}{dt} = \dfrac{1}{V}\left(\dfrac{dn}{dt}\right) = \dfrac{1}{RT}\left(\dfrac{dp}{dt}\right)$

(C) $\dfrac{dC}{dt} = \dfrac{dn}{dt} = \dfrac{V}{RT}\left(\dfrac{dp}{dt}\right)$

(D) None of these.

58. A first order reaction is carried out starting with 10 mol L^{-1} of the reactant. It is 40% complete in 1 h. If the same reaction is carried out with an initial concentration of 5 mol L^{-1}, the percentage of the reaction that is completed in 1 h will be

(A) 40%
(B) 80%
(C) 20%
(D) 60%

59. A first order reaction takes 40 min for 30% decomposition. Calculate $t_{1/2}$.

(A) 77.7 min
(B) 27.2 min
(C) 55.3 min
(D) 67.3 min

60. The number of half-lives ($t_{1/2}$) required to bring the ratio to $N/N_0 = 0.125$ from $N/N_0 = 1$ of a radioactive element is

(A) 2
(B) 4
(C) 3
(D) 1

61. In the study of inversion of sucrose in presence of acid, if r_0, r_t and r_∞ represent the polarimetric readings at times 0, t and ∞, respectively, then at the 50% inversion, which of the following relationship will hold good?

(A) $r_t = r_0 + r_\infty$
(B) $r_t = \dfrac{1}{2}(r_0 + r_\infty)$
(C) $r_t = r_0 - r_\infty$
(D) $r_t = \dfrac{1}{2}(r_0 - r_\infty)$

62. The rate constant, the activation energy and the Arrhenius parameter of a chemical reaction at 25°C are $3.0 \times 10^{-4}\ s^{-1}$, 104.4 kJ mol^{-1} and $6.0 \times 10^{14}\ s^{-1}$, respectively. The value of the rate constant as $t \rightarrow \infty$ is

(A) $2.0 \times 10^{18}\ s^{-1}$
(B) $6.0 \times 10^{14}\ s^{-1}$
(C) ∞
(D) $3.6 \times 10^{30}\ s^{-1}$

63. The half-life for radioactive decay of ^{14}C is 5730 years. An archaeological artifact containing wood had only 80% of the ^{14}C found in a living tree. Estimate the age of the sample.

(A) 1657.3 y
(B) 1845.4 y
(C) 1512.4 y
(D) 1413.1 y

64. Decomposition on NH_3 on heated tungsten yields the following data:

Initial pressure (mm Hg)	65	105	y	185
Half-life (s)	290	x	670	820

What are the values of x and y in that order?

(A) 420 s, 110 mm Hg
(B) 500 s, 160 mm Hg
(C) 520 s, 170 mm Hg
(D) 460 s, 150 mm Hg

65. The rate constant of a certain first order reaction increases by 11.11% per degree rise of temperature at 27°C. By what % will it increase at 127°C, assuming constancy of activation energy over the given temperature range?

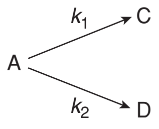
(A) 5.26%
(B) 5.62%
(C) 6.25%
(D) 7.33%

Multiple Correct Choice Type

1. The following statement(s) is (are) correct:

(A) A plot of log K_p vs. $1/T$ is linear.
(B) A plot of log [X] vs. time is linear for a first order reaction, X → P.
(C) A plot of log p vs. $1/T$ is linear at constant volume.
(D) A plot of p vs. $1/V$ is linear at constant temperature.

2. Consider the following case of competing first order reactions.



After the start of the reaction at $t = 0$ with only A, the [Q] is equal to the [D] at all times. The time in which all three concentrations will be equal is given by

(A) $t = \dfrac{1}{2k_1}\ln 3$
(B) $t = \dfrac{1}{2k_2}\ln 3$
(C) $t = \dfrac{1}{3k_1}\ln 2$
(D) $t = \dfrac{1}{3k_2}\ln 2$

3. For a certain reaction A → Products, the $t_{1/2}$ as a function of $[A]_0$, is given as follows:

$[A]_0$ (M)	0.1	0.025
$t_{1/2}$ (min)	100	50

Which of the following is true :
(A) The order is 1/2.
(B) $t_{1/2}$ would be $100\sqrt{10}$ min for $[A]_0 = 1$ M.
(C) The order is 1.
(D) $t_{1/2}$ would be 100 min for $[A]_0 = 1$ M.

4. The polarimeter readings in an experiment to measure the rate of inversion of cane sugar (first order reaction) were as follows

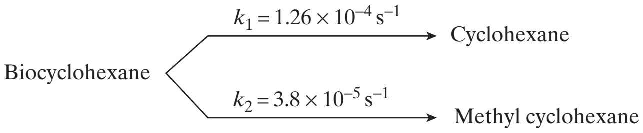
Time (min)	0	30	∞
Angle (degree)	30	20	−15

Identify the true statement(s) [Given that $\log 2 = 0.3, \log 3 = 0.48, \log 7 = 0.84, \ln 10 = 2.3$.]
(A) The half-life of the reaction is 82.71 min.
(B) The solution is optically inactive at 131.13 min.
(C) The equimolar mixture of the products is dextrorotatory.
(D) The angle would be 7.5° at half time.

5. The rate law for the reaction $RCl + NaOH \rightarrow ROH + NaCl$ is given by Rate $= k\,[RCl]$. The rate of this reaction is
(A) is doubled by doubling the concentration of NaOH.
(B) is halved by reducing the concentration of RC1 by one half.
(C) is increased by increasing the temperature of the reaction.
(D) is unaffected by change in temperature.

6. According to adsorption theory of catalysis, the speed of the reaction increases because
(A) the concentration of reactant molecules at the active centers of the catalyst becomes high due to adsorption.
(B) in the process of adsorption the activation energy of the molecules becomes small.
(C) adsorption produces heat which increases the speed of the reaction.
(D) All of the these.

7. Bicyclohexane was found to undergo two parallel first order rearrangements, as given below:


$k_1 = 1.26 \times 10^{-4}\ s^{-1}$
Cyclohexane
Biocyclohexane
$k_2 = 3.8 \times 10^{-5}\ s^{-1}$
Methyl cyclohexane

Choose the correct options:
(A) Percentage of cyclohexane = 77%
(B) Percentage of methylcyclopentane = 23%
(C) Percentage of methylcyclopentane = 77%
(D) Percentage of cyclohexane = 23%

8. If rate of reaction in terms of disappearance of NH_3 is $-d[NH_3]/dt$, for the reaction:

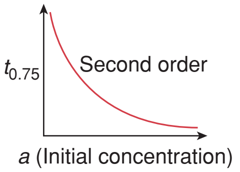
$$4NH_3(g) + SO_2 \rightarrow 4NO_2(g) + 6H_2O(g)$$

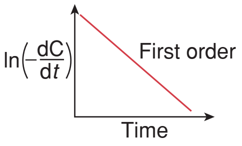
then which of the following expressions are correct for rate of the reaction?

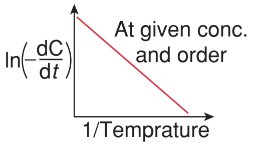
(A) Rate $= -\frac{4}{5}\frac{d[O_2]}{dt}$
(B) Rate $= \frac{3}{2}\frac{d[H_2O]}{dt}$
(C) Rate $= \frac{d[NO]}{dt}$
(D) Rate $= \frac{4}{5}\frac{d[O_2]}{dt}$

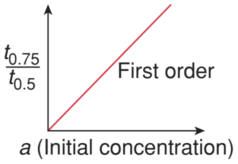
9. Which of the following statements are not true for a catalyst?
(A) It increases the average kinetic energy of the reacting molecules.
(B) It decreases the activation energy.
(C) It alters the reaction mechanism.
(D) It increases the frequency of collisions of the reacting species.

10. Which is the correct graph?

(A)


(B)


(C)


(D)


11. The ozone layer in the earth's upper atmosphere is important in shielding the earth from very harmful ultraviolet radiation. The ozone, O_3, decomposes according to the equation $2O_3(g) \rightarrow 3O_2(g)$. The mechanism of the reaction is through to proceed through an initial fast, reversible step and then a slow second step.

Step 1: Fast, reversible $O_3(g) \rightleftharpoons O_2(g) + O$

Step 2: Slow $O_3(g) + O(g) \rightarrow 2O_2(g)$

Which of the following is correct?
(A) Step 2 is rate determining step.
(B) The rate expression for Step 2 is $-\frac{d}{dt}[O_3] = k[O_3][O]$.
(C) For Step 1, molecularity is 1.
(D) For Step 2, molecularity is 2.

12. Consider the rate law expression for a reaction:

$$\text{Rate} = k[NO_2^-]\,[I^-]\,[H^+]^2$$

Which of the following are true for the reaction?
(A) When concentration of each of H^+, NO_2^- and I^- are tripled, rate becomes nine times.
(B) When concentration of NO_2^- is doubled, of I^- is halved and of H^+ is doubled rate becomes sixteen times.
(C) When concentration of both NO_2^- and I^- are doubled, rate becomes four times.
(D) When concentration of H^+ is tripled, rate becomes nine times.

13. The half-period T for the decomposition of ammonia on tungsten wire was measured for different initial pressures p of ammonia at 25°C. Then

p (mm Hg)	11	21	48	73	120
t (s)	48	92	210	320	525

(A) it is a zero order reaction.
(B) it is a first order reaction.
(C) rate constant for reaction is 0.114 s.
(D) rate constant for reaction is 1.14 s.

Assertion–Reasoning Type

Choose the correct option from the following:

(A) Statement 1 and Statement 2 are true and the Statement 2 is the correct explanation of the Statement 1.
(B) Statement 1 and Statement 2 are true but the Statement 2 is not a correct explanation of the Statement 1.
(C) Statement 1 is true but the Statement 2 is false.
(D) Statement 1 and Statement 2 both are false.

1. **Statement 1:** For a first order reaction, the degree of dissociation is equal to $(1 - e^{-kt})$.
   Statement 2: For a first order reaction, the pre-exponential factor in the Arrhenius equation has the dimension of time^{-1}.
2. **Statement 1:** The reaction N_2 (10 atm) + $3H_2$ (10 atm) → $2NH_3(g)$ is faster.
   Statement 2: Catalyst lowers the activation energy of the reaction.
3. **Statement 1:** For a first order reaction, the concentration of the reactant decreases exponentially with time.
   Statement 2: Rate of reaction at any time depends upon the concentration of the reactant at that time.
4. **Statement 1:** For a second order reaction, graph of [A] vs. t is a straight line.
   Statement 2: For second order reaction, $[A] = kt + \dfrac{1}{[A_0]}$
5. **Statement 1:** The rate constant of a pseudounimolecular reaction has the units of the rate constant of a second order reaction.
   Statement 2: A pseudounimolecular reaction is a reaction of second order in which one of the reactants is present in large excess.
6. **Statement 1:** Molecularity of a reaction cannot be determined experimentally.
   Statement 2: Molecularity is assigned to reactions on the basis of mechanism.
7. **Statement 1:** The order of reaction can have a fractional value.
   Statement 2: The order of reaction cannot be written from the balanced equation of a reaction.
8. **Statement 1:** If the activation energy of a reaction is zero, temperature will have no effect on the rate of reaction.
   Statement 2: Lower the activation energy, faster will be the reaction.
9. **Statement 1:** Molecularlity does not influence the rate of reaction.
   Statement 2: The overall kinetics of a reaction is governed by the slowest step in the reaction scheme.

Comprehension Type

Read the paragraphs and answer the questions that follow.

Paragraph I

The reaction between A and B is of first order with respect to A and of zero order with respect to B. The following data was obtained for four experiments:

Experiment	[A] (M)	[B] (M)	Initial Rate (M min^{-1})
I	0.1	0.1	2.0×10^{-2}
II	x	0.2	4.0×10^{-2}
III	0.4	0.4	y
IV	z	0.2	2.0×10^{-2}

1. The value of x is
   (A) 0.2
   (B) 0.8
   (C) 0.1
   (D) 0.5
2. The value of y is
   (A) 0.2
   (B) 0.08
   (C) 0.1
   (D) 0.5
3. The value of z is
   (A) 0.2
   (B) 0.8
   (C) 0.1
   (D) 0.5

Paragraph II

In 1889, Svante Arrhenius suggested that the relationship between temperature and the rate constant for a reaction obeyed the following equation: $k = Ae^{-E_a/RT}$. For most of the reactions, it was found that the temperature coefficient of the reaction lies between 2 and 3. The activation energy can be calculated from rate constants measured at two temperatures. If the activation energy and the rate constant at a particular temperature are known, the rate constant at another temperature can be calculated. Keeping temperature constant, the effect of catalyst on the activation energy has also been studied by studying how much the rate of reaction changes in the presence of catalyst. Although the catalyst is not part of the overall reaction, it provides a path to the products that has a rate-determining step with a lower activation energy than that of the uncatalyzed reaction.

4. The pre-exponential factor in the Arrhenius equation of a second order reaction has the units
   (A) mol L^{-1}s^{-1}
   (B) L mol^{-1} s^{-1}
   (C) s^{-1}
   (D) It is dimensionless.
5. The activation energy E_a of a reaction can be calculated by plotting:
   (A) k against T
   (B) k against 1/log T
   (C) log k against 1/T
   (D) log k against 1/log T
6. The activation energy of a certain reaction is 87 kJ mol^{-1}. What is the ratio of the rate constants for this reaction when the temperature decreases from 37°C to 15°C?
   (A) 5/1
   (B) 8.3/1
   (C) 13/1
   (D) 24/1
7. The rate of reaction is doubled when the temperature is changed from 298 K to 308 K. What is the energy of activation of the reaction?
   (A) 80 kJ mol^{-1}
   (B) 52.89 kJ mol^{-1}
   (C) 60.28 kJ mol^{-1}
   (D) 58.29 kJ mol^{-1}
8. If x is the fraction of molecules having energy greater than E_a, it will be given by
   (A) $x = -\dfrac{E_a}{RT}$
   (B) $\ln x = -\dfrac{E_a}{RT}$
   (C) $x = e^{E_a/RT}$
   (D) any of these.

Integer Answer Type

The answer is a **non-negative integer**.

1. If the rate constant for the reaction $2A + B \rightarrow C$ was found to be 2.5×10^{-5} L mol^{-1} s^{-1} after 15 s, 2.60×10^{-5} L mol^{-1} s^{-1} after 30 s and 2.55×10^{-5} L mol^{-1} s^{-1} after 60 s, the order of reaction is ________.
2. The order of the following reaction is ________.

   $$CH_2COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$$
3. If the half-life of a reaction is inversely proportional to the cube of initial concentration, the order of reaction is ________.
4. After 24 h, only 0.125 g out of the initial quantity of 1 g of a radioactive isotope remains behind. The half-life period of the radioactive isotope in hours is ________.
5. Starting with an initial pressure of 5 atm of azoisopropane, 40% of it decomposes into nitrogen and hexane vapors in 1 h. The pressure in atmospheres exerted by the mixture in atm at this time will be ________.
6. For a reaction $2A \rightarrow A_2$, the rate of reaction becomes 8 times when the concentration of A changes from a to $3a$. The order of reaction is ________.

Matrix–Match Type

1. Match the problem with its numerical solution.

<table>
<tr><th>Column I</th><th>Column II</th></tr>
<tr><td>(A) If the activation energy is 65 kJ then how much time faster a reaction proceeds at 25°C than at 0°C?</td><td>(p) 5</td></tr>
<tr><td>(B) Rate constant of a first order reaction is 0.0693 min^{-1}. If we start with 20 mol L^{-1}, it is reduced to 2.5 mol L^{-1}, in how many minutes?</td><td>(q) 11</td></tr>
<tr><td>(C) Half-lives of first order and zero order reactions are same. Ratio of rates at the start of reaction is how many times that of 0.693?</td><td>(r) 30</td></tr>
<tr><td>(D) The half-life periods are given as
<table>
<tr><td>[A]$_0$ (M)</td><td>0.0677</td><td>0.136</td><td>0.272</td></tr>
<tr><td>$t_{1/2}$ (s)</td><td>240</td><td>480</td><td>960</td></tr>
</table>
What is the order of the reaction?</td><td>(s) 1/4
(t) 2
(u) 0</td></tr>
</table>

2. Kinetics of hydrolysis of ethyl acetate catalyzed by an acid is followed by titrating a fixed volume of reaction mixture with a standard alkali solution at different intervals of time. V_0, V_1 and V_∞ are the titre values at zero, t and ∞ time. Match the following:

Column I	Column II
(A) $V_0 \propto$	(p) [Acid] as initially present and that formed at time t
(B) $V_1 \propto$	(q) [Acid] present as catalyst
(C) $V_\infty - V_1 \propto$	(r) [Acid] formed after completion reaction
(D) $V_\infty - V_0 \propto$	(s) [Acid] formed after time t

3. Match the quantity with its expression.

Column I	Column II
(A) Half-life of first order reaction	(p) Active mass
(B) Arrhenius equation	(q) $k = Ae^{-E_a/RT}$
(C) Molar concentration	(r) $t_{1/2} = \dfrac{0.693}{k}$
(D) Half-life period of zero under reaction	(s) $\dfrac{a}{2k}$

4. Match the reaction with its order/molecularity.

Column I	Column II
(A) $RCl + H_2O \rightarrow ROH + HCl$	(p) Molecularity 1
(B) $\begin{array}{c}\text{COOH}\\ \vert \\ \text{COOH}\end{array} \longrightarrow CO + CO_2 + H_2O$	(q) Molecularity 3
(C) $2H_2O_2 \rightarrow 2H_2O + O_2$	(r) Molecularity 2
(D) $2NO + Cl_2 \rightarrow 2NOCl$	(s) Molecularity 4

ANSWERS

Review Questions

1. The rate of disappearance of hydrogen is three times the rate of disappearance of nitrogen. The rate of disappearance of N_2 is half the rate of appearance of NH_3.
2. k is a constant called rate constant. x represents the order of reaction.
3. **(a)** $-\dfrac{1}{2}\dfrac{d[NO]}{dt} = -\dfrac{d[O_2]}{dt} = \dfrac{1}{2}\dfrac{d[NO_2]}{dt}$

   (b) $-\dfrac{d[H_2]}{dt} = -\dfrac{d[I_2]}{dt} = \dfrac{1}{2}\dfrac{d[HI]}{dt}$

12. The reaction is first order in O_2 and second order in NO. The overall reaction is third order.
14. E_a is large, k will be small. A small k indicates a slow reaction rate.
15. For a zero order reaction, the half-life for the second reaction will be twice as large as for the first trial. For a first order reaction, the half-life will not change.
17. **(a)** rate $= k_1[A]^2$; **(b)** rate $= k_{-1}[A_2]^1$; **(c)** rate $= k_2[A_2]^1[E]^1$; **(d)** $2A + E \rightarrow B + C$; **(e)** Rate $= k_2\dfrac{k_1}{k_{-1}}[A]^2[E]^1$

Numerical Problems

1. The order is 3

2. Rate = $k[M][N]^2$ where $k = 2.5 \times 10^3$ L^{2}mol^{-2} s^{-1}

3. 18.7 min; 37.4 min

4. 1.72×10^4 y

5. **(a)** Two times; **(b)** No effect

6. **(a)** $-2[A]^{½} = kt + C$; **(b)** Linear with a negative slope; **(c)** $t_{1/2} = \frac{\sqrt{2}(\sqrt{2}-1)}{k}[A]_0^{1/2}$

7. $2p^0 - \frac{(2p^0 - p)^2}{p^0}$

8. 1.21×10^{-2} min^{-1}

9. First, 3.2×10^{-2} min^{-1}

10. 1597.4 years

11. 2.16×10^4

12. 0.926 mol L^{-1}

13. 760 mm Hg

14. 2412.97 s

15. 33.70 h; 67.41 h; 29.78 h

16. **(a)** 0.1667 L mol^{-1} min^{-1}; **(b)** 90 min; **(c)** 30 min

17. 3.2×10^{-2} h^{-1}

18. 4.8×10^{-4} mol L^{-1} s^{-1}

19. 227.1 min

20. 1.58 years

21. 0.019 min^{-1}

22. 4.0×10^{-13}

23. 104 h

24. 52.89 kJ mol^{-1}

Additional Objective Questions

Single Correct Choice Type

1. (C) **2.** (A) **3.** (B) **4.** (C) **5.** (C)
6. (B) **7.** (B) **8.** (C) **9.** (A) **10.** (D)
11. (C) **12.** (D) **13.** (D) **14.** (A) **15.** (B)
16. (D) **17.** (B) **18.** (B) **19.** (D) **20.** (C)
21. (C) **22.** (A) **23.** (A) **24.** (D) **25.** (B)
26. (A) **27.** (A) **28.** (B) **29.** (A) **30.** (C)
31. (A) **32.** (B) **33.** (C) **34.** (B) **35.** (C)
36. (D) **37.** (C) **38.** (C) **39.** (C) **40.** (B)
41. (D) **42.** (D) **43.** (A) **44.** (B) **45.** (D)
46. (C) **47.** (A) **48.** (C) **49.** (A) **50.** (B)
51. (B) **52.** (B) **53.** (A) **54.** (B) **55.** (B)
56. (D) **57.** (B) **58.** (A) **59.** (A) **60.** (C)
61. (B) **62.** (B) **63.** (B) **64.** (D) **65.** (C)

Multiple Correct Choice Type

1. (A, B, D) **2.** (A, B) **3.** (A, B) **4.** (A, B, D) **5.** (B, C)
6. (A, B, C) **7.** (A, B) **8.** (A, C) **9.** (A, D) **10.** (A, B, C)
11. (A, B, C, D) **12.** (A, B) **13.** (A, C)

Assertion–Reasoning Type

1. (B) **2.** (B) **3.** (B) **4.** (C) **5.** (A)
6. (A) **7.** (B) **8.** (B) **9.** (B)

Comprehension Type

1. (A) **2.** (B) **3.** (C) **4.** (B) **5.** (C)
6. (C) **7.** (B) **8.** (B)

Integer Answer Type

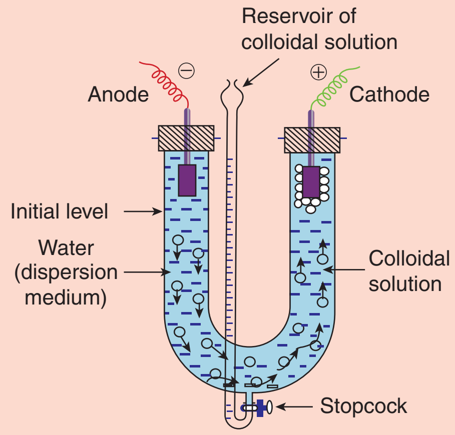
1. (2) **2.** (4) **3.** (4) **4.** (8) **5.** (7)
6. (3)

Matrix–Match Type

1. A → (q); B → (r); C → (t); D → (u)
2. A → (q); B → (p); C → (s); D → (r)
3. A → (r); B → (q); C → (p); D → (s)
4. A → (r); B → (p); C → (r); D → (q)

13

Surface Chemistry



Electrophoresis

Some of the important properties of matter are related to its surface. The surface is an interface between a solid and a gas or a solid and solvent/solute in a solution. It is represented by writing the bulk phases separated by a hyphen, for example, solid-gas, solid-liquid, etc. This interface is only a few molecules thick (e.g., depth of 0.5–2 nm in the solid bulk phase) and its area is determined by the size of particles in the bulk phase. In case of gases, such an interface does not exist as gases are completely miscible. The study of chemical processes that occur at this interface is known as **surface chemistry**. The surface phenomena are responsible for many changes in natural and industrial processes. The applications of surface chemistry are found in catalysis, electrode processes, crystallization and cleansing action of soaps and detergents. However, rusting of iron (corrosion) is an undesirable change occurring at the surface interface which can be prevented by coating the surface with paint, so as to deactivate it from oxidation.

For the accurate study of surface phenomena, it is important that the surface is clean and it has the same composition as the bulk phase. Clean surfaces can be prepared by removal of impurities by heating, chemical reactions or bombardment of electrons/ions. For preparation of absolutely clean surfaces, the metals are subjected to ultra-high vacuum of the order of 10^{-10} to 10^{-14} mm of Hg and then stored under vacuum to prevent contamination by atmospheric gases.

When a molecule strikes a solid surface, it may rebound, undergo a reaction or get adsorbed on the surface. The adsorbed molecule may diffuse on the surface, undergo a reaction or dissolve in the bulk phase. In this chapter, we will focus on the equilibrium and dynamics of processes that occur on the interface and not when the molecule dissolves in the bulk phase.

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13.2 Factors Affecting Adsorption
13.3 Adsorption Isotherms
13.4 Some Applications of Adsorption
13.5 Catalysis
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13.8 Shape-selective Catalysis by Zeolites
13.9 Enzyme Catalysis
13.10 Catalysts in Industry
13.11 Colloids
13.12 Preparation of Colloids
13.13 Purification of Colloidal Solutions
13.14 Properties of Colloidal Solutions
13.15 Coagulation or Precipitation and Hardy–Schulze Rule
13.16 Protection of Colloids
13.17 Emulsions
13.18 Role of Colloids in Natural Phenomena and in Industry

13.1 | ADSORPTION

The phenomenon of the assimilation of higher concentration of any species at the surface of a solid or liquid as compared to that present in the bulk of the material is known as **adsorption**. Some examples of adsorption are: the accumulation of dust/soot on our skin when we travel in regions of heavy traffic with the car windows rolled down; protection from poisonous gases particularly in coal mines using gas masks, etc.

In the process of adsorption, substances partition in a manner that they leave the gaseous or liquid phases and form a new layer on the surface of a solid substrate.

The solid or liquid on whose surface gas or liquid is adsorbed is called **adsorbent** or **substrate**; it must be a condensed phase, that is, either liquid or solid. Solids in finely divided state have large surface areas and can act as good adsorbents, for example, silica gel, metals, clay, etc. The adsorbents (charcoal or a mixture of products) used in the gas mask adsorb poisonous gases and prevent their inhalation. The gas or solution which is held to this surface is called **adsorbate**; it is atomic, ionic or molecular; generally a liquid or a gas. Adsorption can be positive or negative. When the concentration of the adsorbate is more on the surface of the adsorbent than in the bulk, it is termed as **positive adsorption**. When the concentration of the adsorbate is less on the surface of the adsorbent than in the bulk, it is termed as **negative adsorption**.

Adsorption and Related Phenomena

Adsorption is a surface phenomenon and it differs from absorption, which *is a bulk phenomenon in which the concentration of molecular species is uniformly distributed throughout the body of the solid or liquid.* In adsorption, the concentration of the adsorbate increases only on the surface, whereas it increases uniformly throughout the bulk phase in case of absorption (Fig. 13.1). The differences between the two phenomena are tabulated in Table 13.1.

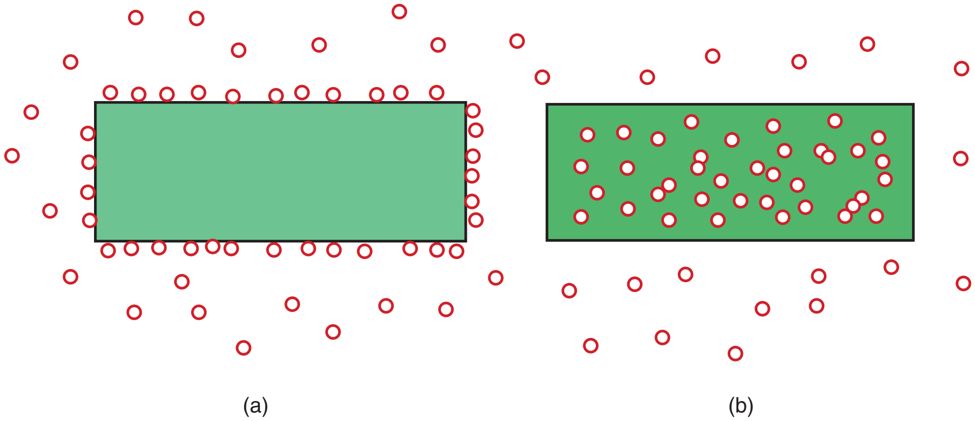

(a) (b)

Figure 13.1 Diagrammatic representation of (a) adsorption and (b) absorption.

Table 13.1 Difference between adsorption and absorption

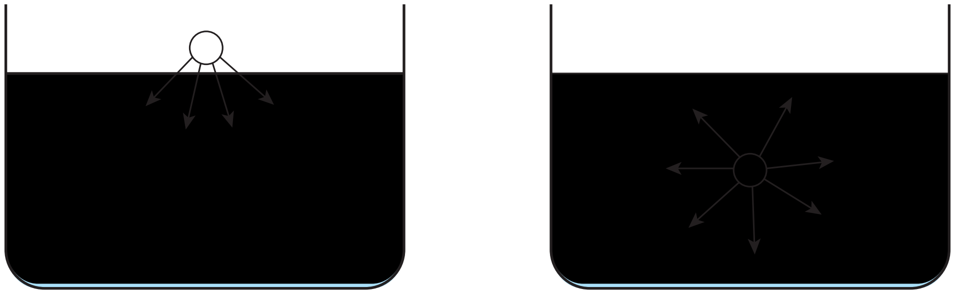
Absorption	Adsorption
Absorption is a bulk phenomenon in which the concentration of molecular species is uniformly distributed throughout the body of the solid or liquid.	The phenomenon of assimilation of higher concentration of any species at the surface of a solid or liquid as compared to that present in the bulk of the material.
Slower process and the attainment of equilibrium takes longer time.	Faster process and attainment of equilibrium takes shorter time.
For example, ammonia is absorbed by water, whereas it is adsorbed by charcoal.	For example, adsorbents (charcoal or a mixture of products) used in the gas mask adsorb these gases and prevent their inhalation.

The term **sorption** is used to describe a process in which both absorption and adsorption takes place while *desorption* is used to describe a process opposite to sorption. For example, when a chalk is dipped in ink, the color in the ink is adsorbed on the surface, while the solvent is absorbed in the entire thickness of the chalk. Similarly, in preparation of a curry, the yellow coloring compounds of turmeric are absorbed in the curry while they are adsorbed on the surface of the pan in which the curry is being cooked, thus imparting it yellow stains.

Desorption is the phenomenon whereby a substance is released from or through a surface, and it occurs when the concentration (or pressure) of the substance in bulk phase is lowered. This process takes place by either increasing the temperature or reducing the pressure. The role of desorption is important in catalysis, where it is used to make the surface of the solid catalyst free for the fresh adsorption of the reactants on the surface.

Adsorption Mechanism

The driving force for the process of adsorption is the presence of unbalanced or residual forces at the solid or liquid surface. These arise because the molecules present at the surface are attracted by other molecules only from below (net inward force) and from the sides unlike the molecules inside the bulk phase which are attracted uniformly from all sides (Fig. 13.2). The molecules on the surface thus tend to move inwards where forces of attraction are uniform from all sides. As a result of these residual forces, the surface of the solid or liquid is in a state of strain and has a tendency to attract and retain molecules of another species, thus creating an excessive concentration at the surface. Adsorption reduces these residual forces, and this results in a decrease in the surface energy which appears in the form of heat. This is known as heat of adsorption and the process of adsorption is an **exothermic process**.



(a) (b)

Figure 13.2 Mechanism for (a) adsorption and (b) absorption.

The incoming molecule of adsorbate faces two kinds of interactions from the substrate. These are electronic repulsions and steric restrictions from the adsorbent surface. If the substrate is an aromatic or unsaturated species, the charge donated during the formation of an adsorption bond is conducted away from the location of adsorption, thus reducing electronic repulsion for the incoming adsorbate molecule. In a non-conducting adsorbent, such delocalization of charge is not possible and most of the donated charge lies close to the site of adsorption, thus restricting the approach of more adsorbent molecules.

The phenomenon of adsorption is spontaneous and so the free energy (ΔG) of the system should be negative.

(13.1)

Since process of adsorption restricts the movement of gas molecules, it is always accompanied by a decrease in the entropy (ΔS). Since adsorption is an exothermic process, the enthalpy change (ΔH) of the system is also negative. For ΔG to be negative, it follows that ΔH must be sufficiently higher than ΔS so that the value of ($\Delta H - T\Delta S$) becomes negative. As the adsorption proceeds, ΔH becomes less and less negative and at $\Delta H = T\Delta S$, ΔG becomes zero and an equilibrium is reached. In the equilibrium state, the process of adsorption and desorption proceed at the same rate.

Note: The molecule of adsorbate must approach the substrate from within a certain cone-shaped area above the vacant adsorption site, otherwise steric restriction would prevent successful adsorption.

Physisorption and Chemisorption

On the basis of the forces of attraction between the adsorbent and the adsorbate, adsorption can be classified into two types

1. **Physisorption**, also known as physical adsorption or van der Waals adsorption. For example, adsorption of gases by charcoal.
2. **Chemisorption**, also called chemical adsorption or activated adsorption. For example, adsorption of oxygen on tungsten is an example of chemisorption.

In some processes, the two types of adsorptions may occur simultaneously or may interchange their form at different temperature conditions. For example, in hydrogenation of alkenes, nickel is used as the catalyst. Initially, hydrogen gas undergoes physisorption on the nickel surface, and at low temperatures dissociates to form hydrogen atoms that are bonded to the nickel by hydride formation. Similarly, if silica gel and elemental bromine are placed at the two ends of a sealed container, the bromine vapors travel to silica gel and are chemisorbed on the surface of silica. When the chemisorbed monolayer is complete, the successive layers of bromine are adsorbed by physisorption.

The enthalpy of chemisorption is more than the enthalpy of physisorption because of strong chemical bonds that are involved in chemisorption, whereas in case of physisorption there are weak van der Waals forces involved. Since formation of these bonds requires higher energy of activation, this adsorption is also called **activated adsorption**.

The extent of physisorption and chemisorption depends on the nature of adsorbent. At a given temperature and pressure, greater the surface area per unit mass of the adsorbent, greater is the adsorption on its surface. Finely divided solids having a large surface area show a much larger extent of adsorption. This is because more and more residual forces are created on the surface when a substance of larger size is divided into smaller units.

In physisorption, the nature of the adsorbate also affects the extent of adsorption. In general, easily liquefiable gases, that is, gases with high critical temperatures, are more readily adsorbed because van der Waals forces are stronger near the critical temperature. The general features and differences between the two types of adsorption are summarized in Table 13.2.

Table 13.2 Distinguishing features of physisorption and chemisorption

Physisorption	Chemisorption
Forces of attraction involved between adsorbent and adsorbate are weak, long-range van der Waals forces.	Forces of attraction involved between adsorbent and adsorbate are strong chemical bonds.
No formation of a surface complex.	Formation of a surface complex between adsorbate and adsorbent.
Reversible in nature, as the gas adsorbed can be recovered back by lowering pressure or raising the temperature.	Irreversible in nature because it involves formation of chemical bonds between adsorbent and adsorbate.
The adsorbent does not show preference for any specific gas. It can bond similarly by van der Waals forces to all the gases. It is shown by almost all gases.	Since the process of adsorption involves formation of chemical bonds, it is highly specific in nature. Chemisorption takes place only where there is possibility of formation of chemical bonds between the adsorbent and adsorbate.
Occurs at low temperatures due to low activation energy (~5 kJ).	Occurs at high temperatures due to high activation energy.
Magnitude of adsorption decreases with increase in temperature.	Magnitude of adsorption increases with increase in temperature.
Equilibrium is attained rapidly on changing temperature and pressure.	Equilibrium is attained relatively slowly.
Heat (enthalpy) of adsorption is low (20–40 kJ).	Heat (enthalpy) of adsorption is high (80–240 kJ mol^{-1}).
Adsorption is generally multilayered.	Adsorption is monolayered.

Solved Example 13-1

Why is adsorption accompanied by a decrease in both enthalpy as well as entropy of the system?

Solution

Since the process of adsorption restricts the movement of gas molecules, it is always accompanied by a decrease in the entropy (ΔS). Since adsorption is an exothermic process, the enthalpy change (ΔH) of the system is also negative.

Solved Example 13-2

The enthalpy of chemisorption is more than the enthalpy of physisorption. Why?

Solution

The enthalpy of chemisorption is more than the enthalpy of physisorption because of strong chemical bonds that are involved in chemisorption, whereas in case of physisorption there are weak van der Waals forces involved.

Solved Example 13-3

Why is adsorption always exothermic?

Solution

The above statement can be explained in two ways.

(a) Adsorption leads to a decrease in the residual forces on the surface of the adsorbent. This causes a decrease in the surface energy of the adsorbent. Therefore, adsorption is always exothermic.

(b) When a gas is adsorbed on a solid surface, its movement is restricted leading to a decrease in the entropy of the gas, that is, ΔS is negative. Now for a process to be spontaneous, ΔG should be negative. From $\Delta G = \Delta H - T\Delta S$, we find that since ΔS is negative, ΔH has to be negative to make ΔG negative. Hence, adsorption is always exothermic.

Solved Example 13-4

What is the state of ΔH and ΔS when bromine gas gets adsorbed on charcoal?

Solution

When bromine gas gets adsorbed on charcoal, then heat is liberated. Therefore, the enthalpy change is negative. Thus, ΔH = negative and the entropy change ΔS = negative.

13.2 | FACTORS AFFECTING ADSORPTION

Adsorption of Gases on Solids

Adsorption of gases on the surface of a solid is very common and is sometimes referred to as occlusion. A common example is the adsorption of ammonia by charcoal. The amount of gas adsorbed depends upon the nature of gas as well as the surface area of the adsorbent. Greater the surface area, greater are the residual forces on the surface and higher is the magnitude of adsorption of the gas on the surface. Adsorbate is adsorbed to a different extent by different adsorbents under the same conditions and by the same adsorbents under different conditions. Adsorption of gases on solids depends upon the following factors.

1. **Temperature:** Adsorption is always accompanied by evolution of heat, so according to Le Chatelier's principle, the magnitude of adsorption should increase with a decrease in temperature. Also, when the temperature of the system is lowered, then due to smaller thermal energy, more number of molecules are held to the surface by residual forces and hence higher is the adsorption. A curve showing variation of adsorption with temperature at constant pressure is known as **adsorption isobar**.

   The change in rate of adsorption with temperature is different for physisorption and chemisorption. In fact, it has been actually found that an increase in temperature tends to cause a decrease in the magnitude of adsorption at a constant pressure in case of physisorption. In chemisorption since it requires some activation energy, the magnitude of adsorption increases initially and then decreases with an increase in temperature. This effect can be depicted graphically by adsorption isobars as shown in Figs. 13.3(a) and (b) where (x/m) denotes the amount of gas adsorbed per unit mass of adsorbent and T the temperature.

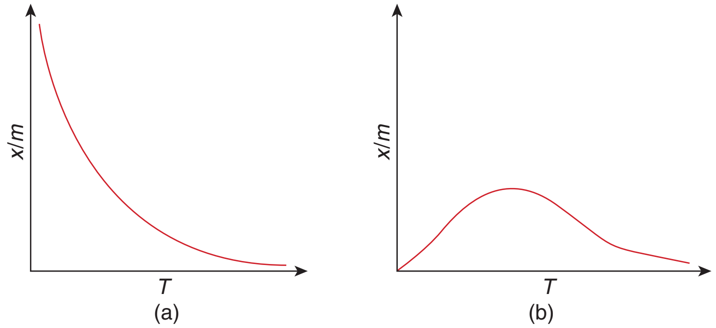


Figure 13.3 Effect of temperature on adsorption at constant pressure: (a) Physisorption and (b) chemisorption.

Note: A plot of temperature vs. pressure for a given amount of adsorption is called adsorption isostere. This plot should yield a linear graph.

2. **Pressure:** The variation of adsorption with pressure at a given constant temperature can be depicted graphically as adsorption isotherms in Fig. 13.4. At a constant temperature, the extent of adsorption increases with an increase in pressure at low pressure values. This is in agreement with Le Chatelier's principle which states that the system would move towards lesser number of molecules with an increase in pressure. Physical adsorption increases with increase in pressure. The extent of adsorption is expressed as x/m where x is amount of adsorbate, m is mass of adsorbent when dynamic equilibrium is established between free gas and the adsorbed gas. More about adsorption isotherms is discussed in Section 13.3.
3. **Nature of adsorbent:** At ature and pressure, greater the surface area per unit mass of the adsorbent, greater is the adsorption on its surface. Finely divided solids having a large surface area show a much larger extent of adsorption. This is because more and more residual forces are created on the surface when a substance of larger size is divided into smaller units.

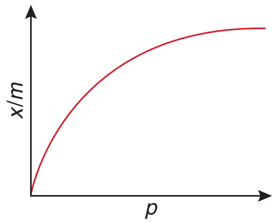


Figure 13.4 Effect of pressure on adsorption at constant temperature.

4. **Nature of adsorbate:** Adsorption depends upon the nature of adsorbate. In case of gases, the molecular forces involved in adsorption are more predominant in the easily liquefiable and readily soluble gases (e.g., HCl, NH_3, Cl_2) so the adsorption of such gases is higher than the permanent gases (e.g., H_2, N_2, O_2).
5. **Surface area:** The extent of adsorption increases with the increase in surface area of the adsorbent. The greater the surface area, more will be the extent of adsorption. This is the reason why porous or finely divided forms of adsorbents adsorb larger quantities of adsorbate.

Adsorption of Solids from Solutions

Solids are known to adsorb solutes from solutions. For example, acetic acid is adsorbed from a mixture of acetic acid and water when shaken with charcoal. The concentration of acetic acid in solution decreases. Similarly, litmus solution when shaken with charcoal becomes colorless. A number of factors influence the adsorption of solutes from solution by solids and they are listed as follows:

1. An adsorbent adsorbs certain solute from solution in preference to others. The extent of adsorption depends on the nature of the adsorbent as well as adsorbate. This extent is usually greater for solutes with high molecular mass.
2. Adsorption of a solute decreases with rise in temperature due to increase in the kinetic energy of solute particles, thereby causing these particles to leave the surface. The shape of an adsorption isotherm in solution phase depends on the choice of adsorbate, substrate temperature and the nature of the solvent.

3. Adsorption of solutes from a solution increases with increase in the concentration of solution. When the solute is adsorbed by an adsorbent, it is called **positive adsorption** (e.g., adsorption of KCl by charcoal from a concentrated solution); whereas when the solvent is taken up by the adsorbent, it is called **negative adsorption** (e.g., adsorption of water by charcoal from a concentrated solution of KCl).
4. The extent of adsorption increases with the increase in surface area of the adsorbent.
5. Adsorption increases as the solubility of the solute in a solvent decreases. Also, adsorption strength increases with an increase in the analyte polarity (polarity of solute).

Solved Example 13-5

Can physisorption transform into chemisorption at high temperature?

Solution

As physisorption requires very low activation energy compared to chemisorption, so physisorption can be transformed into chemisorption only at high temperatures.

Solved Example 13-6

How does the rate of physisorption vary with **(a)** decrease in temperature; **(b)** increase in pressure and **(c)** increase in surface area?

Solution

According to physisorption,

$$\text{Absorbate} + \text{Absorbent} \rightarrow \text{Gas/Solid} + \text{Heat}$$

According to Le Chatelier's principle, decrease in temperature will shift the equilibrium to right or rate of physisorption will increase. On increasing the pressure, the equilibrium will shift in the direction in which there is decrease in number of moles (i.e., in forward direction). Adsorption increases with increase in surface area.

Solved Example 13-7

How do size of particles of adsorbent, pressure of gas and prevailing temperature influence the extent of adsorption of a gas on a solid?

Solution

Adsorption of a gas on a solid depends on:

(a) **Size of particles of adsorbent:** Smaller the size of the colloid particle, larger is the surface area and thus greater is the adsorption.

(b) **Pressure of gas:** At constant temperature, adsorption reaches equilibrium at higher pressures, that is, at high pressure, adsorption is independent of pressure. However, it increases with increase in pressure before attaining equilibrium.

(c) **Temperature:** In physical adsorption, it decreases with increase in temperature. However, in chemisorptions, it increases initially and then decreases.

Solved Example 13-8

Why is it essential to wash the precipitate with water before estimating it quantitatively?

Solution

When a substance gets precipitated, some ions from the electrolyte that combine to form the precipitate get adsorbed on the surface of the precipitate. Therefore, it becomes important to wash the precipitate before estimating it quantitatively in order to remove these adsorbed ions or other such impurities.

Solved Example 13-9

Out of CO and NH_3 which is adsorbed on activated charcoal to a large extent and why?

Solution

Ammonia (NH_3) is adsorbed on activated charcoal to a large extent because more easily liquefiable gas undergoes adsorption to a greater extent. Also ammonia has a higher critical temperature than CO and a stronger intermolecular force of attraction.

13.3 | ADSORPTION ISOTHERMS

Adsorption isotherm determines the variation in the amount of gas adsorbed by the adsorbent at a particular temperature by varying the pressure. Different gases exhibit different types of isotherms on adsorption on different adsorbents. These can be broadly categorized into five types as depicted in Fig. 13.5. Type I corresponds to unimolecular adsorption, while Types II–V correspond to multimolecular adsorption.

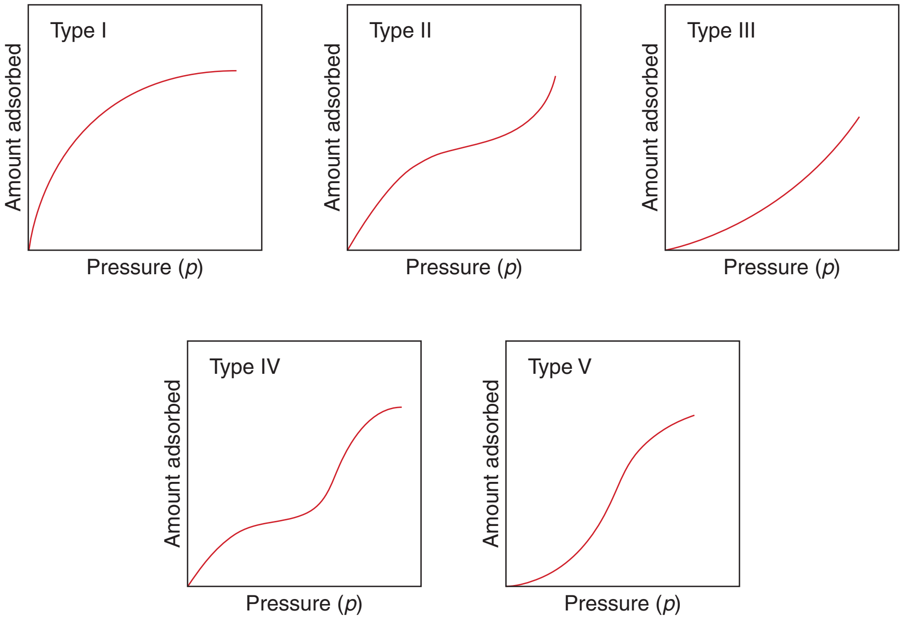


Figure 13.5 Adsorption isotherms.

Freundlich Adsorption Isotherm

Freundlich first observed the variation between extent of adsorption and pressure at constant temperature. His observation was depicted by plotting mass of gas adsorbed per gram (x/m) of the adsorbent against pressure (p) at constant temperature [Fig. 13.6(a)]. The curves in Fig. 13.6(b) show that for a given pressure, the extent of physisorption decreases with increase in temperature. The curves become flat as we approach higher pressures suggesting that adsorption reaches a saturation point.

Note: The shape of an adsorption isotherm in gaseous phase depends on the choice of adsorbate, substrate and temperature.

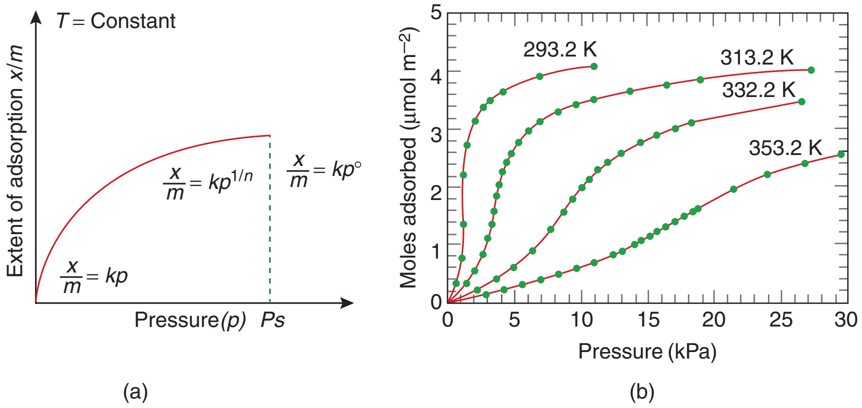


Figure 13.6 Extent of adsorption vs. pressure at (a) constant temperature and (b) different temperatures.

From the given plot it is clear that at pressure p_s, (x/m) reaches the maximum value. p_s is called the saturation pressure. Three cases arise from the graph now.

Case 1 – At low pressure: The plot is straight and sloping, indicating that the pressure is directly proportional to (x/m), that is,

$$(x/m) \propto p \Rightarrow \frac{x}{m} = kp$$

where x is the mass of the adsorbate and m is the mass of the adsorbent at pressure p; k is constant depending upon the nature of adsorbate and adsorbent.

Case 2 – At high pressure: When pressure exceeds the saturated pressure, (x/m) becomes independent of p values.

$$\frac{x}{m} \propto p^0 \Rightarrow \frac{x}{m} = kp^0$$

Case 3 – At intermediate pressure: In this case, (x/m) depends on p raised to the powers between 1 and 0, that is, fractions. This relationship is known as the **Freundlich adsorption isotherm**.

$$\frac{x}{m} \propto p^{1/n} \Rightarrow \frac{x}{m} = kp^{1/n} \quad (n > 1)$$

The value of n is usually greater than 1 and so the increase in adsorption is not as rapid as the increase in pressure.

Now taking log on both sides, we get

$$\log\frac{x}{m} = \log k + \frac{1}{n}\log p$$

On plotting the graph between log (x/m) and log p, a straight line is obtained with the slope equal to $1/n$ and the intercept equal to log k (Fig. 13.7).

The relation between pressure and extent of adsorption explained by Freundlich's isotherm is approximate. It holds good for a limited range of pressure but fails at higher pressures. The factor $1/n$ can have values varying between 0 and 1. When $1/n = 0$, x/m is constant and when $1/n = 1$, x/m varies directly with pressure. These observations are supported by experimental results. However, as the pressure increases, the actual extent of adsorption (experimental isotherm) approaches saturation. Hence, the relation does not hold good at high pressures. Some other limitations of Freundlich isotherm are:

1. It is only applicable for physical adsorption and does not account for multilayer adsorption.
2. It does not consider the role of surface area of adsorbent in the process of adsorption.

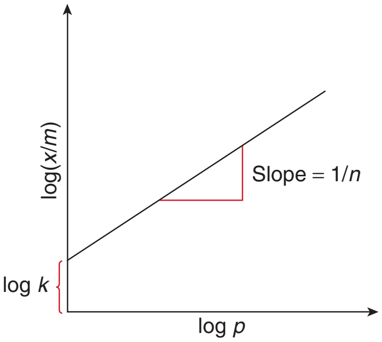


Figure 13.7 Freundlich adsorption isotherm.

Freundlich adsorption isotherm is also applicable to solutions by replacing the pressure term by the concentration (C) of adsorbates in solutions. The relationship is modified as follows

$$\frac{x}{m} = kC^{(1/n)} \tag{13.2}$$

Taking logarithm, it becomes
$$\log\left(\frac{x}{m}\right) = \log k + \frac{1}{n}\log C \tag{13.3}$$

A graph between log (x/m) and log C is a straight line for small ranges of concentrations.

Solved Example 13-10

In an adsorption experiment, a graph between log (x/m) vs. log p was found to be linear with a slope of 45°. The intercept on the log (x/m) axis was found to be 0.3010. Calculate the amount of the gas adsorbed per gram of charcoal under a pressure of 0.5 atm.

Solution

Using Freundlich isotherm equation $x/m = kp^{1/n}$. Taking log on both the sides, we get

$$\log\frac{x}{m} = \log\ k + \frac{1}{n}\log\ p$$

Comparing it with a general straight line equation, we get slope = $1/n$ and intercept = log k. Given that slope = tan θ where $\theta = 45°$. Now,

$$\tan 45° = 1 = \frac{1}{n} \Rightarrow n = 1$$

Intercept = 0.3010 (given). Therefore, log k = 0.3010 ⇒ $k = 2$.

It is also given that $p = 0.5$ atm, so

$$\frac{x}{m} = kp^{1/n} = 2 \times (0.5)^1 = 1.0$$

Solved Example 13-11

Check the applicability of Freundlich adsorption isotherm for the adsorption of solute on a solid at 25°C and find the values of k and n.

Concentration (mol L^{-1})	0.05	0.10	0.50	1.00	1.50
(x/m) (g)	0.048	0.072	0.144	0.192	0.228

Solution

Using the given data and the following expressions

$$\frac{x}{m} = kC^{1/n}$$

$$\log(x/m) = \log k + \frac{1}{n}\log C$$

we can plot log C on x-axis and log (x/m) on y-axis. The slope gives value of $1/n$ and the intercept gives value of log k. Calculate k and n as 0.19 and 2.29, respectively.

Solved Example 13-12

Different concentrations of aqueous solutions placed with charcoal which adsorbs a part of solute from solution as reported below at equilibrium.

Concentration of solution × 10^{-2}	2.0	4.0
x/m	0.185	0.290

Calculate the values of log k and n.

Solution

$$\log\left(\frac{x}{m}\right) = \log k + \left(\frac{1}{n}\right)\log C$$

$$\log 0.185 = \log k + \left(\frac{1}{n}\right)\log(2 \times 10^{-2})$$

$$\log 0.290 = \log k + \left(\frac{1}{n}\right)\log(4 \times 10^{-2})$$

Solving, we get $x = 0.64$, $k = 83.5$ and log $k = 1.92$.

Langmuir Adsorption Isotherm

In 1916, Langmuir gave an expression to determine the extent of adsorption depending on variation in pressure, based on the following assumptions:

1. The surface of solid consists of only a fixed number of adsorption sites.
2. All the sites are equivalent and the surface is homogeneous.
3. Each site can adsorb only one gas molecule. Adsorption is monolayered, that is, gases adsorbed onto the surface can form a layer of only one molecule in thickness.
4. The heat of adsorption is constant and identical for all the adsorption sites.
5. The gas molecules adsorbed do not interact with each other.
6. The gas molecules have a tendency to get adsorbed on the surface of the solid, and the adsorbed molecules have a tendency to evaporate back (desorb) into the gas phase.

Based on above assumptions, he stated that the rate of desorption is proportional to the concentration of adsorbed molecules, that is, to the fraction θ of the surface already covered by gas molecules. So,

$$\text{Rate of desorption} = k_d\theta$$

where k_d is a constant. The rate of adsorption is proportional to pressure of the gas as well as the fraction of surface uncovered $(1 - \theta)$. So,

$$\text{Rate of adsorption} = k_a p(1-\theta)$$

where k_a is a constant. Now at equilibrium:

$$\text{Rate of adsorption} = \text{Rate of desorption}$$

$$k_a p(1-\theta) = k_d\theta \tag{13.4}$$

$$k_a p - k_a p\theta = k_d\theta \Rightarrow k_a p = \theta(k_d + k_a p) \Rightarrow \theta = \frac{k_a p}{k_d + k_a p}$$

or

$$\theta = \frac{(k_a/k_d)p}{1+(k_a/k_d)p} \tag{13.5}$$

Substituting k_a/k_d by k_1, which is a constant known as distribution constant, we get

$$\theta = \frac{k_1 p}{1+k_1 p} \tag{13.6}$$

We also know that θ is proportional to the amount of gas adsorbed (x) per unit mass of the adsorbent (m)

$$\frac{x}{m} = k_2\theta \tag{13.7}$$

where k_2 is another constant. Substituting the value of θ from Eq. (13.6) into Eq. (13.7):

$$\frac{x}{m} = \frac{k_1 k_2 p}{1+k_1 p} \tag{13.8}$$

This is known as the **Langmuir equation**. Taking the reciprocal of Eq. (13.8), we get

$$\frac{1}{(x/m)} = \frac{1+k_1p}{k_1k_2p} = \frac{1}{k_1k_2p} + \frac{1}{k_2} \tag{13.9}$$

$$\frac{p}{(x/m)} = \frac{1}{k_1k_2} + \frac{p}{k_2} \tag{13.10}$$

A plot of $p/(x/m)$ versus p gives a straight line with a slope of $(1/k_2)$ and intercept of $(1/k_1k_2)$ from which the values of k_1 and k_2 can be calculated.

Langmuir monolayer adsorption isotherm explains the nature of the adsorption isotherm given by Freundlich (Fig. 13.6) under the following conditions:

1. When the pressure of the gas is low, the amount of gas adsorbed is directly proportional to the pressure of the gas. This is because at low pressure, adsorption is lower and θ can be considered to be negligible in comparison to 1 so Eq.(13.4) can be written as:

$$k_a p = k_d \theta$$

or
$$\theta = \frac{k_a p}{k_d} = k_1 p \tag{13.11}$$

Substituting the expression of θ in Eq. (13.7), we get

$$\frac{x}{m} = k_1k_2p \tag{13.12}$$

2. When pressure is high, adsorption attains a constant value. This is because at high pressure, adsorption of the gas is high and θ can be considered close to 1 so Eq. (13.4) can be written as:

$$k_a p(1-\theta) = k_d \Rightarrow (1-\theta) = \frac{k_d}{k_a p}$$

or
$$\theta = \frac{1-k_d}{k_a p} = 1 - \frac{1}{k_1 p} \tag{13.13}$$

Substituting expression of θ in Eq. (13.7), we get

$$\frac{x}{m} = k_2 - \frac{k_2}{k_1 p} \tag{13.14}$$

At high value of pressure, k_2/k_1p becomes very small and so:

$$\frac{x}{m} = k_2 \tag{13.15}$$

3. When the pressure is intermediate, the extent of adsorption does not increase as fast as the pressure. This can be explained on the fact that the value of denominator increases faster than the numerator on increasing the value of pressure in the Langmuir equation, $x/m = k_1k_2\,p/(1 + k_1p)$.

Multilayer Adsorption

Langmuir adsorption isotherm has certain limitations because it is based on the assumption that adsorption is monoolayered and that the adsorbed molecules do not interact with each other. This is true only at low pressure and high temperature. This is because at low pressure, lesser number of molecules strike the surface; while at higher temperature, molecules have higher thermal energy and prevent multilayer formation. However, at high pressure and low temperature, additional layers are formed and the Langmuir model is no longer valid. Brunauer, Emmett and Teller proposed a theory (BET theory) to explain multilayer adsorption. As in Langmuir's isotherm, the theory assumes that the solid surface possesses uniform, localized sites and that adsorption on one site does not affect adsorption on neighboring sites. After the formation of first layer, the molecules can continue to be adsorbed on subsequent layers (second, third, … and nth layer). The surface area available for the nth layer is the same as that for the coverage of the $(n-1)$th layer. Based on these assumptions, the equation for the ratio of the volume (V) of gas adsorbed to the volume (V_m) required to form a monolayer is derived as

$$\frac{V}{V_\mathrm{m}}=\frac{Cx}{(1-x)[1+(C-1)x]} \tag{13.16}$$

Here, $x = p/p_\mathrm{o}$, where p is the pressure of the gas at temperature T and p_o is the saturated vapor pressure of the gas at the same temperature. The equation may also be written in the form

$$\frac{x}{V(1-x)}=\frac{1}{CV_\mathrm{m}}+\frac{(C-1)x}{CV_\mathrm{m}} \tag{13.17}$$

It is possible to determine the parameters V_m and C from plot of $x/V(1-x)$ versus x and thus get the volume of gas required to form a monolayer.

Determination of Surface Area of Solids

The adsorption of gases by a solid surface can be used to determine the surface area of solids. If a monolayer is formed, then the fractional surface area covered is given by the ratio of the volume V of the gas adsorbed to the volume V_m required to form the monolayer, assuming that volumes are at the same temperature and pressure. Equation (13.6) may also be expressed as

$$V=\frac{V_\mathrm{m}}{1+1/k_1p}$$

If the gases follow Langmuir's isotherm, the parameters V_m and k_1 can be determined from slope and intercept of the plot $1/V$ versus $1/p$.

However, deviations occur in Langmuir equation, especially at the higher pressures and BET multilayer adsorption equation, Eq. (13.16) may be used for determination of V_m. The surface area occupied by a single molecule of adsorbate on the surface can be estimated from density of liquefied adsorbate. Nitrogen gas is commonly used for surface area determination at its boiling point (−195°C) and assuming the molecules are spherical and closely packed. The area of one molecule of nitrogen under these conditions is taken as 16.2×10^{-20} m^2.

Solved Example 13-13

The data below are for the adsorption of CO on charcoal at 273 K. Confirm that they fit the Langmuir isotherm and find **(a)** the constant k_1 and volume corresponding to complete surface coverage **(b)** the fraction of surface covered at $p = 600$ mm Hg and **(c)** change of standard free energy on adsorption at STP.

p (mm Hg)	100	200	30	400	500	600	700
V (cm^3)	10.2	18.6	25.5	31.4	36.9	41.6	46.1

Mass of sample of charcoal = 3.022 g.

Solution

(a) For determination of k_1 and V_max, the given data can be modified to include p/V, so that from the equation

$$\frac{p}{V}=\frac{p}{V_\mathrm{max}}+\frac{1}{k_1V_\mathrm{max}}$$

a graph can be plotted between p/V and p to obtain the slope as $1/V_\mathrm{max}$ and the intercept as $1/k_1V_\mathrm{max}$.

p (mm Hg)	100	200	30	400	500	600	700
V (cm^3)	10.2	18.6	25.5	31.4	36.9	41.6	46.1
p/V (mm Hg cm^{-3})	9.8	10.75	1.17	12.74	13.55	14.42	15.18

The graph obtain is shown in Fig. 13.8.

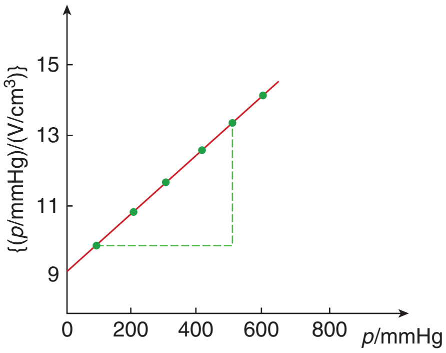


Figure 13.8

The slope ($1/V_{max}$) is obtained as 0.009. So, V_{max} = 111.11 cm^3 and the intercept is 9 $\Rightarrow k_1 = 0.009/9 = 0.001$ mm Hg^{-1}.

(b) At 600 mm Hg, the fractions of surface area covered is $\theta = \dfrac{V}{V_{max}} = \dfrac{41.6}{111.11} = 0.374$.

(c) We know that $\Delta G_{ads} = -2.303RT\log k_1$. Substituting the value of $k_1 = 0.001$ mm $Hg^{-1} = 0.76$ atm^{-1}, we get

$$\begin{aligned}\Delta G_{ads} &= -2.303RT\log(0.76)\\ &= 0.119\times 2.303\times 8.314\times 273\\ &= 0.62 \text{ kJ mol}^{-1}\end{aligned}$$

Solved Example 13-14

The adsorption of a gas is described by Langmuir adsorption isotherm. Calculate the pressure at which the fractional coverage is **(a)** 0.1, **(b)** 0.5 and **(c)** 0.95. Given k_1 = 0.9 kPa^{-1} at 27°C.

Solution

We know that $\theta = \dfrac{k_1 p}{1+k_1 p} \Rightarrow p = \left(\dfrac{\theta}{1-\theta}\right)\dfrac{1}{k_1}$. Therefore,

(a) $p = \left(\dfrac{0.1}{0.9}\right)\times\dfrac{1}{0.9} = 0.123$ kPa

(b) $p = \left(\dfrac{0.5}{0.5}\right)\times\dfrac{1}{0.9} = 1.11$ kPa

(c) $p = \left(\dfrac{0.1}{0.05}\right)\times\dfrac{1}{0.9} = 21.11$ kPa

Solved Example 13-15

In a solution of 100 mL 0.5 M acetic acid, 1 g of active charcoal is added, which absorbs acetic acid. It is found that the concentration of acetic acid becomes 0.49 M. if surface area of charcoal is 3.01×10^2 m^2, calculate the area occupied by single acetic acid molecule on the surface of charcoal. **(IIT-JEE 2003)**

Solution

The number of moles of acetic acid in 100 mL (before adding charcoal) = 0.05 mol

The number of moles of acetic acid in 100 mL (after adding charcoal) = 0.049 mol

The number of moles of acetic acid adsorbed on the surface of charcoal = 0.05 – 0.049 = 0.001 mol

The number of molecules of acetic acid adsorbed on the surface of charcoal = $0.001\times 6.02\times 10^{23} = 6.02\times 10^{20}$

Given that the surface area of charcoal = 3.01×10^2 m^2, so the area occupied by single acetic acid molecule on the surface of charcoal is

$$\frac{3.01\times 10^2}{6.02\times 10^{20}} = 5\times 10^{-19}\text{ m}^2$$

13.4 | SOME APPLICATIONS OF ADSORPTION

Some industrial applications of adsorption are as follows:

1. **In pollution control and clarification of sugar in food industry:** Activated carbon or activated charcoal is an extremely porous carbon that has a very large surface area available for adsorption or chemical reactions. It is the most widely used adsorbent for preparing gas masks to selectively adsorb toxic gases, in pollution control system for the treatment of volatile organic compounds in effluent air based on the nature of chemicals and adsorbents,

removal of organic matter from drinking water, decoloration of vinegar and sugar solution, and control of odors in the food industry.

2. **In filtration:** Molecular sieve contains tiny pores of uniform size that act as an adsorbent for gases and liquids. It can be considered to be a filter operating on the molecular level. Small molecules which can pass through the pores are absorbed, whereas large molecules are not. Since water molecules are small enough to pass through molecular sieves, these can function as a desiccant and absorb water up to about 22% of its own weight.
3. **In controlling humidity and drying air:** Silica is used for drying of processed air (e.g., oxygen, natural gas) and adsorption of hydrocarbons from natural gas. Silica and alumina gels have been employed for drying of air and controlling humidity in rooms. Adsorption chillers are filled with silica gel onto which hot water/steam coming from industrial sources can be adsorbed.
4. **In metallurgy:** Fuller's earth is used in refining of petroleum and vegetable oil; it adsorbs unwanted materials.
5. **In dying industry:** Mordants like alum are used to adsorb the dye particles in the dying industry.
6. **In paint industry:** The dissolved gases from the paint are removed during manufacture by suitable adsorbents to increase their adherence capacity. Moreover, all surfaces are layered with gaseous, liquid or solid films that are removed just before the paint is applied. This is done by suitable liquids called wetting agents which adsorbs these films. For example, spirit acts as a wetting agent in furniture painting.
7. **In chromatography:** Adsorption chromatography is a technique used for the separation of compounds based on their selective adsorption on the surface of a suitable adsorbent. When a solvent containing a mixture of solutes is made to pass through an adsorbent, solutes get separated in different layers of the adsorbent with the solute most readily adsorbed in the initial layers and less readily adsorbed in the later layers. This principle is used in the separation of solution by column chromatography, gas chromatography and high performance liquid chromatography.
8. **In catalysis:** Adsorption plays an important role in catalysis as a number of manufacturing industrial chemical processes are heterogeneous catalyst reactions. The adsorbent (catalyst) should be covered by the reactants in order to be catalytically active. The interaction of reactants or products with the surface should be neither too strong nor too weak. If the adsorption is too weak, the catalyst has little effect. If the strength of the bond between the adsorbent and adsorbate is high, the adsorbate molecules may be immobilized on the surface and the reactants may fail to react with each other, thus decreasing the activity of the catalyst. Thus the activity of a catalyst increases initially and then decreases with the strength of adsorption. Some manufacturing processes which are carried out in the presence of heterogeneous catalysts are as follows:

   Synthesis of ammonia by Haber's process using iron as a catalyst: $N_2 + 3H_2 \xrightarrow{\text{Fe}} 2NH_3$.

   Nickel is used as a catalyst in the hydrogenation of vegetable oils: $\text{Vegetable oil} + H_2 \xrightarrow{\text{Ni}} \text{Vegetable ghee}$.
9. **In titrations as indicators:** Certain dyes which are useful in adsorption also find use as indicators in precipitation titrations. For example, KBr is easily titrated with $AgNO_3$ using eosin as an indicator.
10. **In softening hard water:** Ion exchange adsorption is defined as the process of release of a particular type of ion and adsorption of other types of ions by the adsorbent. It involves the chemical reaction between ions in solution and that of the solid adsorbent, which in turn releases replacement ions into the solution. Such adsorbents known as ion exchange resins are insoluble, cross-linked, long-chain polymers with microporous structure having functional groups attached to their chains; for example, zeolites, clay and soil humus. Ion exchange resins are being used for various environmental applications and pollution abatement processes, such as water softening, demineralization, desalination, removal of ammonia, removal of heavy metals, radioactive waste treatment, etc.
11. **In removal of colored impurities:** Colored impurities can be removed from solutions by passing through a bed of charcoal. For example, white sugar crystals are obtained by passing solution of sugar crystals containing colored impurities over a bed of charcoal. The coloring substances get adsorbed on the charcoal bed.
12. **In production of vacuum:** After evacuating the vessels using a vacuum pump, they are further treated with adsorbents such as charcoal to remove traces of air. Similarly, adsorbent materials may be used between two layers of Dewar flasks/containers to remove all trapped air.
13. **In separation of inert gases:** A mixture of noble gases can be separated based on the difference in extent of adsorption on charcoal.
14. **In biological applications:** The phenomenon of adsorption is used to remove toxins such as germs, etc., from the body. It is also used for the recovery and concentration of vitamins and other biological substances.

13.5 | CATALYSIS

Many reactions can be accelerated by the presence of small amount of substances, which themselves remain unaltered chemically during the course of reaction. Such substances are called **catalysts**. The action of the catalyst is specific for a reaction.

Though the amount of catalyst should be unchanged at the end of the reaction, it enters into the chemical reaction and forms a complex with any of the reactants. The complex is an intermediate and undergoes decomposition to give the products of the reaction with the regeneration of the catalyst molecule.

An extremely small amount of a catalyst will cause a considerable increase in the rate of a reaction. For example, a small quantity of MnO_2 will increase the rate of decomposition of $KClO_3$ appreciably. Since the catalyst remains unchanged at the end of the reaction, it does not give energy to the system. Therefore, it has no influence on the position of equilibrium. This has been verified experimentally.

There are two types of catalysts based on the activity:

1. **Positive catalyst or accelerator:** The catalyst changes the speed of the reaction by making available a path other than the one which is followed by the reaction in the absence of the catalyst. If path is such that in the presence of the catalyst, molecules with lower energy can participate in the reaction, the speed of the reaction is increased. Such a catalyst which accelerates the rate of a reaction is called *positive catalyst* or *accelerator*. The examples are as follows:

$$2SO_2(g) + O_2(g) \xrightarrow{Pt} 2SO_3$$
$$N_2(g) + 3H_2(g) \xrightarrow{Fe} 2NH_3(g)$$

2. **Negative catalysts or inhibitors:** There are certain substances which, when added to the reaction mixture, retard its reaction rate instead of increasing it. These are called *negative catalysts* or *inhibitors*. The examples of this type are antifreezes like glycerol which retards rusting of the machine; lead tetraethyl or nickel carbonyl acts as antiknock material in the internal combustion engines; and small quantity of alcohol retards oxidation of chloroform.

The substances affecting the activity of catalysts are as follows:

1. **Promoters:** The presence of a small quantity of some substance called promoters, activates the catalyst. For example, molybdenum promotes the activity of iron catalyzing synthesis of ammonia.
2. **Anitcatalysts:** Those substances which deactivate the catalyst are called anticatalysts.
3. **Poisons:** Those substances which decrease the efficiency of the catalyst and the reaction thus stops at the first stage of reduction. For example, when $BaSO_4$ and quinolone are added to acetylene, they act as poisons. This means that reaction will stop at ethene and ethane will not be formed.

$$\underset{\text{Acetylene}}{C_2H_2 + H_2} \rightarrow \underset{\text{Ethene}}{CH_2{=}CH_2} + H_2 \xrightarrow{Pt} \underset{\text{Ethene}}{C_2H_6}$$

$$\underset{\text{Acetylene}}{C_2H_2 + H_2} \xrightarrow{Pd + BaSO_4 + \text{quinoline}} \underset{\text{Ethene}}{CH_2{=}CH_2}$$

Characteristics of Catalysts

The characteristic properties of catalyst are listed as follows:

1. The catalyst remains unchanged in its composition and amount at the end of the reaction. However, it may undergo some change in its physical form; for example, the solid catalyst used may be recovered in powdered form.
2. A small amount of catalyst is enough to promote a chemical reaction in most of the reactions. However, in certain homogeneous reactions, the rate of reaction may depend upon the concentration of catalyst.
3. A catalyst does not affect the thermodynamic parameters of a chemical reaction, such as enthalpy, entropy or free energy change.
4. The use of catalyst does not shift the equilibrium of the reaction as it affects rates of both forward and backward reactions to the same extent.
5. The ability of a catalyst to affect the rate of a reaction is known as its **activity**. An effective catalyst is one that can adsorb the reactant molecule strongly enough for *them* to react but not so strongly that the product molecules

adhere permanently to the surface of the catalyst. Chemisorption is the main factor in deciding the activity of a catalyst. The adsorption of reactants on the catalyst surface should be neither too strong nor too weak. It should just be strong enough to make the catalyst active. The activity of catalyst is significant in the hydrogenation reactions and in formation of water. Storing hydrogen and oxygen together will not result in formation of water without the presence of a catalyst. Use of platinum as catalyst enhances the rate of reaction to a great extent:

$$2H_2(g) + O_2(g) \xrightarrow{Pt} 2H_2O(l)$$

Note: The metals of Groups 5 to 11 show an increasing order of catalytic activity in hydrogenation reaction.

6. The ability of a catalyst to affect the rate of certain reaction and prevent the other side reactions is known as **selectivity** of the catalyst. The catalyst thus directs the reaction to yield the desired products in improved yields. This is also known as specificity of the catalyst, which implies that the use of a catalyst is specific to a reaction. For example, by using different catalysts, we can get different products for the reaction between H_2 and CO.

$$CO(g)+3H_2(g) \xrightarrow{Ni} CH_4(g)+H_2O(g)$$

$$CO(g)+2H_2(g) \xrightarrow{Cu/ZnO-CrO_3} CH_3OH(g)$$

$$CO(g)+H_2(g) \xrightarrow{Cu} HCHO(g)$$

Solved Example 13-16

How does a catalyst increase the rate of a chemical reaction?

Solution

Catalyst is defined as a substance which alters the rate of a chemical reaction without affecting the equilibrium or the nature of products. The catalyst reacts with the reactants to form an intermediate complex which readily undergoes decomposition to yield the product and the catalyst is regenerated. It lowers the activation energy of the reaction.

Solved Example 13-17

Discuss the role of adsorption and desorption in catalysis.

Solution

The surface of the catalyst has active sites on which one or more reactants get adsorbed in the form of a unimolecular layer because of some unsatisfied valence forces of the catalyst. If both the reactant molecules are adsorbed on the surface, the reaction takes place readily due to the close proximity of the reactants. If one reactant molecule is attached to the surface, then it may be hit by the other reactant moving freely as a gas or liquid. The products formed are desorbed, that is, they leave the surface of the catalyst which is regenerated and the active sites are again available for reaction.

Solved Example 13-18

20% surface sites have adsorbed N_2. On heating N_2 gas evolved from sites and was collected at 0.001 atm and 298 K in a container of volume is 2.46 cm^3. Density of surface sites is 6.023×10^{14} cm^{-2} and surface area is 1000 cm^2, find out the number of surface sites occupied per molecule of N_2. **(IIT-JEE 2005)**

Solution

Given that $p_{N_2} = 0.001$ atm, $T = 298$ K, $V = 2.46$ cm^3. By ideal gas equation, we have $pV = nRT$. So,

$$n = \frac{pV}{RT} = \frac{0.001\times 2.46\times 10^{-3}}{0.0821\times 298} = 1.0\times 10^{-7}$$

Now, molecules of $N_2 = 6.023\times 10^{23}\times 1\times 10^{-7} = 6.023\times 10^{16}$

Also, the total sites available $= 6.023 \times 10^{14} \times 1000 = 6.023 \times 10^{17}$. Therefore, surface sites used to adsorb N_2 is

$$20\% \text{ of the total sites available} = \frac{20}{100} \times 6.023 \times 10^{17} = 12.04 \times 10^{16}$$

Therefore, the sites occupied per molecule of N_2 is

$$\frac{\text{Surface sites used to adsorb } N_2}{\text{Molecules of } N_2} = \frac{12.04 \times 10^{16}}{6.02 \times 10^{16}} = 2$$

Solved Example 13-19

Name two physical quantities that remain unaffected when a reversible reaction is carried out in the presence of a catalyst.

Solution

A catalyst has effect neither on the relative energies of the reactants and products, nor on the equilibrium constant, K_{eq}. It merely speeds up the reaction, thus allowing it to reach equilibrium more quickly. Thus, the two physical quantities that remain unaffected when a reversible reaction is carried out in the presence of a catalyst are enthalpy change and equilibrium constant.

13.6 | TYPES OF CATALYTIC REACTIONS

The catalysis process may be classified as follows:

1. **Homogeneous catalysis:** In this catalytic reaction, the catalyst is in the same phase as the reactants. In the gaseous phase, an example of homogeneous catalysis is the use of NO to accelerate the reaction between CO(g) and O_2(g). The reactants and the catalysts are in the same gaseous phase.

$$2CO(g) + O_2(g) \xrightarrow{NO(g)} 2CO_2(g)$$

   In solution phase, the example of homogeneous catalysis is ester hydrolysis in acidic medium. For example, acidic hydrolysis of ethyl acetate.

$$CH_3CH_2COOCH_3(l) + H_2O(l) \xrightarrow{HCl(l)} CH_3CH_2COOH(aq) + CH_3OH(aq)$$

2. **Heterogeneous catalysis:** In this catalytic reaction, the catalyst is in a different phase from the reactants. The simplest example of this is the reaction between ethylene and hydrogen in the presence of a nickel catalyst. The reactants are gases whereas the catalyst is a solid.

$$CH_2 = CH_2 + H_2 \xrightarrow{Ni} CH_3CH_3$$

   Ethene molecules are adsorbed on the surface of the nickel. The double bond between the carbon atoms breaks and the electrons are used to bond it to the nickel surface. Similarly, a solid platinum or V_2O_5 catalyzes the oxidation of SO_2 to SO_3 in contact process for the manufacture of H_2SO_4 and solid iron is used as a catalyst in manufacture of ammonia by Haber's process. Another example is gold acting as catalyst in the following reaction:

$$2N_2O \xrightarrow{Au} 2N_2 + O_2$$

   Here gold acts as a catalyst. The N_2O is chemically adsorbed on the metal surface. A bond is formed between the O of the N_2O and an Au atom. This weakens the bond joining O to N, thus making it easier for the molecule to break apart.

3. **Autocatalysis:** When a product formed in the course of reaction speeds up the reaction, the phenomenon is called autocatalysis. For example, the hydrolysis of an ester by water is an autocatalytic process, since the acid liberated as a result of hydrolysis catalyzes the reaction.
4. **Induced catalysis:** In this catalytic reaction, one reaction influences the rate of another reaction that does not occur under ordinary conditions. For example, the reduction of $HgCl_2$ by oxalic acid proceeds at a much faster rate in the presence of $KMnO_4$. This is because the reduction of $KMnO_4$ by oxalic acid further induces the reduction of $HgCl_2$.
5. **Acid–base catalysis:** Some reactions are catalyzed by the presence of an acid or a base and this is known as acid–base catalysis. Some examples are:
   (a) Hydrolysis of an ester

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + H_2O \xrightarrow{[H^+]} CH_3COOH + C_2H_5OH$$

(b) Inversion of cane sugar

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{[H^+]} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

6. **Enzyme catalysis:** Reactions catalyzed by enzymes are termed enzyme catalysis. Enzymes are highly complex, non-living, nitrogenous organic substances produced by living animals and plants. This catalysis is discussed in detail in Section 13.9.

13.7 | THEORY OF HETEROGENEOUS CATALYSIS

A catalytic process in which the catalyst and the reactants are present in different phases is known as a heterogeneous catalysis. An example of heterogeneous catalysis is the synthesis of ammonia from hydrogen and nitrogen by the Haber process.

$$N_2(g) + 3H_2(g) \xrightarrow{Fe(s)} 2NH_3(g)$$

The reaction takes place on the surface of an iron catalyst that contains traces of aluminium and potassium oxides. It is thought that hydrogen molecules and nitrogen molecules dissociate while being held on the catalytic surface. The hydrogen atoms then combine with the nitrogen atoms to form ammonia. Finally, the completed ammonia molecule breaks away, freeing the surface of the catalyst for further reaction. This sequence of steps is illustrated in Fig. 13.9. It is important to remove CO in the synthesis of ammonia as CO adversely affects the activity of the iron catalyst, used in Haber's process.

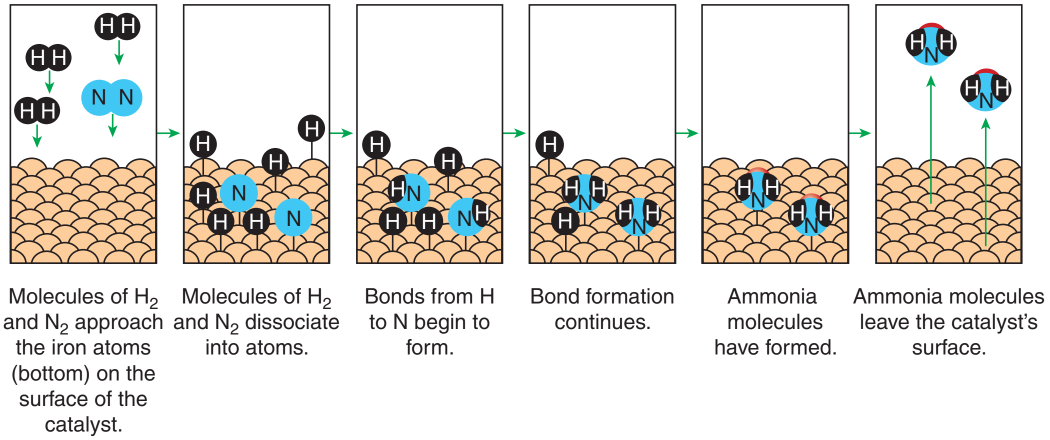

H H
N N
H
N
Molecules of H_2 and N_2 approach the iron atoms (bottom) on the surface of the catalyst.
Molecules of H_2 and N_2 dissociate into atoms.
Bonds from H to N begin to form.
Bond formation continues.
Ammonia molecules have formed.
Ammonia molecules leave the catalyst's surface.

Figure 13.9 Haber's process.

The theories used to explain the catalytic action are as follows:

1. **Intermediate compound theory:** According to the earliest theory suggested to explain the catalytic action, the catalyst forms a reactive and unstable intermediate with a reactant. This intermediate readily reacts with the other reactant to form the product and the catalyst is obtained back in its original form. This can be represented as follows:

$$A + B \longrightarrow C + D$$
$$\text{Step 1: } A + X \longrightarrow C + AX \text{ (intermediate compound)}$$
$$\text{Step 2: } AX + B \longrightarrow D + X$$

2. **Adsorption theory:** A later theory explained the mechanism for heterogeneous catalytic action and the theory has been further modified over the years to explain the observed characteristics of catalytic reactions. According to this theory, the surface of the catalyst has active sites on which one or more reactants get absorbed in the form of a unimolecular layer because of some unsatisfied valence forces of the catalyst. If both the reactant molecules are

absorbed on the surface, the reaction takes place readily due to the close proximity of the reactants. If one reactant molecule is attached to the surface, it may be hit by the other reactant moving freely as a gas or liquid. The products formed are desorbed, that is, they leave the surface of the catalyst which is regenerated and the active sites are again available for reaction. The steps involved in the mechanism of heterogeneous catalysis are listed as follows:

(a) Diffusion of the reactant molecules on the surface of the catalyst.

(b) Adsorption of reactant molecules at the active sites on the surface of the catalyst.

(c) Formation of an intermediate complex between a reactant and the catalyst. Further reaction of the intermediate complex with the other reactant to form products.

(d) Desorption of the products from the surface of the catalyst and regeneration of the catalyst.

(e) Diffusion of reaction products away from the surface of the catalyst.

3. Combination of the two theories: Both the above theories were combined to describe the catalytic action.

(a) The catalyst provides an alternative path for a reaction by reacting with the reactants to form an adsorbed activated complex. The reaction proceeds through lowering of activation energy.

(b) The active centers on the surface of the catalyst play an important role in governing the amount of adsorption. The number of active sites can be increased by powdering the catalyst and increasing its surface area, by increasing the roughness of the catalyst's surface, or by preparing the catalyst in colloidal form. The enhanced activity of finely powdered catalyst can be explained by the increased surface area and hence increased number of active sites. Similarly, catalysts with rough surfaces are more effective due to greater number of active sites in the cracks, corners and breaks in the rough surface.

(c) Many transition metals and their compounds act as catalysts. The catalytic activity is due to their ability to exhibit multiple oxidation states and to provide larger surface area for adsorption. They form unstable intermediate compounds and provide a new path with lower activation energy. For example, V_2O_5 is used in Contact process to manufacture sulphuric acid.

This mechanism accounts for most of the observed characteristics of the catalytic reactions and explains why the amount and composition of a catalyst remains unchanged at the end of the reaction. It, however, cannot explain the action of catalytic promoters and poisons.

Solved Example 13-20

Write the reaction in which bismuth molybdate is used as a catalyst. Explain which characteristic of catalyst is shown by this reaction.

Solution

The reaction of oxidation of propene to acrolein and acrylonitrile in the presence of bismuth molybdate $Bi_2(MoO_4)_3$ is shown in Fig. 13.10.

In this selective oxidation, the slow step that controls the overall reaction rate and which is desired to catalyze, is activation of the first C–H bond. With these two-component catalysts, the first step, breaking the C–H bond, is catalyzed by the more basic oxide, for example, bismuth oxide. Molybdenum is involved in the next step – activation of a second hydrogen and insertion of an oxygen atom into the organic molecule. In this step, molybdenum is reduced. Reduced molybdenum is re-oxidized by oxygen from the feed. The catalysis depends on the ability of oxomolybdenum species to cycle between the VI and IV oxidation numbers, in the process releasing and transferring an oxygen atom:

$$Mo^{VI}O_2 \rightleftharpoons Mo^{IV}O + O$$

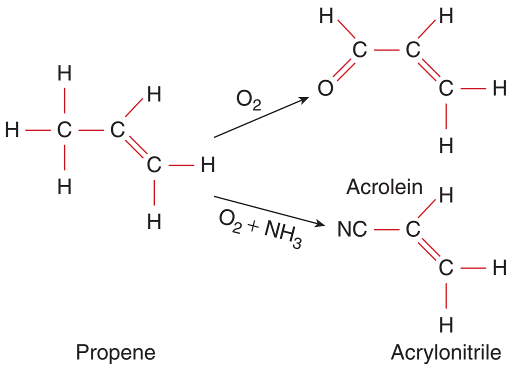


Figure 13.10

13.8 | SHAPE-SELECTIVE CATALYSIS BY ZEOLITES

Shape-selective catalysts are those catalysts whose reactions depend on the pore structure of the catalyst and the size of the reactant and product molecules. In such reactions, zeolites are commonly used as catalysts because the size of reactants and/or products selectively fit into the pores and cavities of the zeolite.

Zeolites are naturally occurring hydrated aluminosilicates of the general formula $M_{x/n}[(AlO_2)_x \cdot (SiO_2)_y] \cdot m\ H_2O$ where *n* is the charge of the metal cation, M^{n+}. M is usually Na^+, K^+ or Ca^{2+} and *m* is the number of moles of water of hydration, which is highly variable. The characteristic of zeolites is the openness of the honeycomb-like $[(Al_2)O_2]_n$ network. They consist of a three-dimensional network of silicates in which some sites have been replaced by aluminium atoms, giving rise to a Al–O–Si network.

The zeolites have pores of various sizes and act as molecular sieves for the reactants. To achieve this, zeolites are heated in vacuum so that the water of hydration is lost. Once the water is removed, the zeolite structure becomes porous. The pore size in zeolites is generally in the range 260–740 pm. The size of the porous cavities influences the catalytic activity of the catalyst. Only those molecules can be adsorbed in the pores whose sizes are small enough. This facilitates the molecules to enter the cavities and leave easily. Hence, zeolites act as selective adsorbents.

Zeolites are used for purification of water but their use as ion-exchange materials have been replaced by synthetic cationic and anionic exchange resins. However, they continue to be used as selective adsorbents for gases or liquids. A large number of zeolites are now prepared synthetically to meet specific catalyst requirements. For example, a synthetic zeolite ZSM-5 with formula $Na_nAl_nSi_{96-n}O_{192}\cdot 16H_2O$ is specifically designed for use in petroleum industry. It is used to bring about dehydration of alcohols to convert them directly into a mixture of hydrocarbons that can be used as petrol with high octane number.

Solved Example 13-21

Some zeolites are used to separate long straight chain hydrocarbons from branched chain hydrocarbons in a petrochemical industry. Explain how this separation is possible.

Solution

Zeolites are usually microporous. The pore size varies between 260 and 740 pm. Thus, only the molecules that are very small in size can be adsorbed by them. The larger molecules are not able to enter the pores. Thus, zeolites act as selective adsorbents or as molecular sieves. It is for this reason that sodium aluminium silicate can absorb straight chain hydrocarbons and not branched chain or aromatic ones. Hence, zeolites are used to separate long straight chain hydrocarbons from branched chain hydrocarbons in a petrochemical industry.

13.9 | ENZYME CATALYSIS

Complex nitrogenous compounds which are produced by living plants and animals are known as enzymes. Enzymes are biological macromolecules, most being proteins or complex nitrogenous compounds, that catalyze numerous reactions in the bodies of animal and plants to maintain the life processes. They are thus called **biochemical catalysts** and their action is **biochemical catalysis**. Some examples of enzyme-catalyzed reactions include:

1. Inversion of cane sugar into glucose and fructose with enzyme invertase:

$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}(aq)} + H_2O \xrightarrow{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6(aq)} + \underset{\text{Fructose}}{C_6H_{12}O_6(aq)}$$

2. Conversion of glucose into ethanol with enzyme zymase:

$$C_6H_{12}O_6(aq) \xrightarrow{\text{Zymase}} 2C_2H_5OH(aq) + 2CO_2(g)$$

3. Conversion of starch into maltose with enzyme diastase:

$$2\underset{\text{Starch}}{(C_6H_{10}O_5)_n}(aq)+nH_2O\xrightarrow{\text{Diastase}}\underset{\text{Maltose}}{nC_{12}H_{22}O_{11}}(aq)$$

4. Hydrolysis of urea with enzyme urease:

$$NH_2CONH_2(aq) + H_2O(l)\xrightarrow{\text{Urease}}2NH_3(g) + CO_2(g)$$

5. Conversion of milk into curd by lactobacilli enzyme present in the curd used for setting.
6. Digestion of food by enzyme ptyalin in the saliva.
7. Conversion of proteins into peptides in the stomach with enzyme pepsin and conversion of proteins into amino acids in intestine with enzyme trypsin.

Enzymes show far greater **specificity** for their reactants (called **substrates**) and for their products than shown by most chemical catalysts. For example, in the enzymatic synthesis of proteinspolypeptides consisting of well over 1000 amino acid residues are synthesized virtually without error. Similarly, the enzyme maltase catalyzes the reaction of maltose and water to form glucose but has no effect on the other two common disaccharides sucrose and lactose.

Note: Common names for enzymes are formed by adding the suffix -*ase* to the root of the substrate name. For example, the derivations of maltase, sucrase and lactase from maltose, sucrose, and lactose. However, many enzymes particularly digestive enzymes, have common names such as pepsin, rennin, trypsin, and so on.

Characteristic Features of Enzymes

The characteristics of enzymes as catalysts are as follows:

1. Enzymes show high specificities towards their physiological substrates; compounds that differ only slightly from the natural substrate are often not acted upon.
2. The activity of many enzymes can be finely tuned in the presence of activators and coenzymes, allowing the metabolism to proceed at an optimal rate for the well-being of the organism.
3. They have the ability to bring about vast increases in the rates of reactions; in most instances, the rates of enzyme-catalyzed reactions are faster than those of uncatalyzed reactions by factors of 10^6–10^{12}. For example, the enzyme rate constant k_{cat} for decarboxylation of the amino acid arginine is 7×10^{19} times larger than the rate constant for the spontaneous decarboxylation of amino acids.
4. They are efficient as they permit reactions to take place at reasonable rates, even under the mild conditions that exist in living cells (i.e., approximately neutral pH and a temperature of about 35°C.)
5. They are influenced by inhibitors and poisons.

Mechanism of Enzyme Catalysis

Louis Pasteur (1822–1895) was one of the first scientists to study enzyme-catalyzed reactions. He believed that living yeasts or bacteria were required for reactions such as conversion of glucose to alcohol by yeasts. In 1897, Eduard Büchner (1860–1917) made a cell-free filtrate that contained enzymes prepared by grinding yeast cells with very fine sand. The enzymes in this filtrate converted glucose to alcohol, thus proving that the presence of living cells is not required for enzyme activity. For this work, Büchner received the Nobel Prize in Chemistry in 1907.

Enzymes act according to the following general sequence. Enzyme (E) and substrate (S) combine to form an enzyme – substrate intermediate (E – S). This intermediate decomposes to give the product (P) and regenerate the enzyme. The mechanism can be represented as

$$E+S \underset{k_{eq}}{\rightleftharpoons} E-S \overset{k}{\rightarrow} E+P$$

The second step is the rate determining step, so,

$$\text{Rate} = k[E-S]$$

For the hydrolysis of maltose, the sequence is

$$\underset{(\mathrm{E})}{\text{Maltase}} + \underset{(\mathrm{S})}{\text{Maltose}} \rightleftharpoons \underset{(\mathrm{E-S})}{\text{Maltase}-\text{Maltose}}$$

$$\underset{(\mathrm{E-S})}{\text{Maltase}-\text{Maltose}} + \mathrm{H_2O} \rightarrow \underset{(\mathrm{E})}{\text{Maltase}} + \underset{(\mathrm{P})}{2\text{Glucose}}$$

The steps involved in the enzyme catalyzed reactions are:

1. The substrate is bound to the protein (generally all enzymes are proteins) and the reaction takes place at what is called the **active site**. The amino acids located in the active site are arranged so that they can interact specifically with the substrate. Non-covalent forces such as van der Waals forces, electrostatic forces, hydrogen bonding and hydrophobic interactions, bind the substrate to the active site.
2. The enzyme and the substrate combine to form an **enzyme–substrate complex**. Formation of the complex often induces a conformational change in the enzyme that allows it to bind the substrate more effectively. This is called an **induced fit**.
3. The binding of substrate causes certain of its bonds to become strained, and therefore, break more easily. The product of the reaction usually has a different shape from the substrate, and this altered shape causes the complex to dissociate to yield the product and regenerated enzyme.
4. The enzyme can then accept another molecule of the substrate, and the whole process is repeated:

$$\text{Enzyme} + \text{Substrate} \leftrightarrow \text{Enzyme} - \text{Substrate complex} \leftrightarrow \text{Enzyme} + \text{Product}$$

Lock-and-Key Hypothesis

It was Emil Fischer's discovery in 1894 of the ability of enzymes to distinguish between α- and β-glycosidic linkages that led him to formulate his **lock-and-key hypothesis** for enzyme specificity. According to this hypothesis, the specificity of an enzyme (the lock) and its substrate (the key) comes from their geometrically complementary shapes.

Enzyme specificity is thus believed to be due to the particular shape of a small part of the enzyme, its active site, which exactly fits a complementary-shaped part of the substrate (see Fig. 13.11). When the substrate and the enzyme come together, they form a substrate–enzyme complex unit. The substrate, activated by the enzyme in the complex, reacts to form the products, regenerating the enzyme.

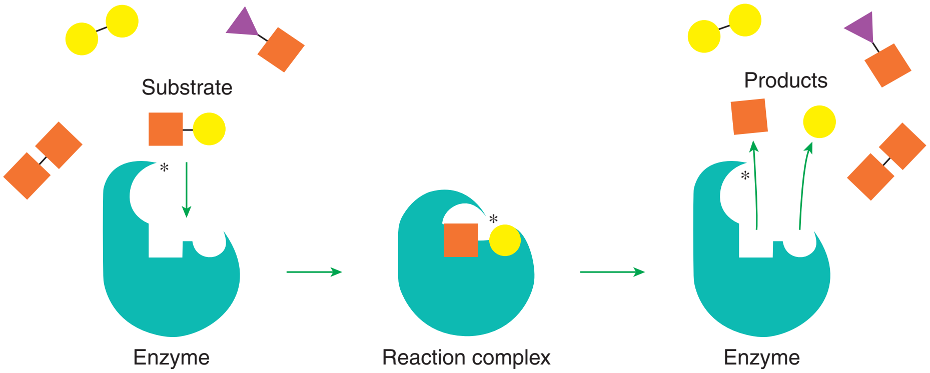


Figure 13.11 Enzyme–substrate interaction illustrating specificity of an enzyme by the lock-and-key model.

Induced-Fit Model

A more recent model of the enzyme–substrate catalytic site, is the **induced-fit model**. It visualizes a flexible site of enzyme–substrate attachment, with the substrate inducing a change in the enzyme shape to fit the shape of the substrate. This model allows for the possibility that in some cases the enzyme might wrap itself around the substrate and so form the correct shape of lock and key. Thus, the enzyme does not need to have an exact preformed catalytic site to match the substrate.

Note: The flexible nature of enzyme helps explain enzyme binding specificity and the ability of enzyme to convert reactants into products. An enzyme is a dynamic catalyst.

Solved Example 13-22

Give the names of the enzymes that catalyze the hydrolysis of **(a)** urea, **(b)** invert sugar, **(c)** maltose.

Solution

The enzymes are **(a)** urease, **(b)** invertase and **(c)** maltase.

Solved Example 13-23

Explain the enzyme action in hydrolysis of protein in stomach and enzyme.

Solution

In the stomach, the enzyme pepsin forms while its precursor pepsinogen reacts with HCl. Hydrolysis occurs due to both pepsin and HCl, and the peptide bonds are broken.

In the intestine, hydrolysis occurs due to digestive enzymes trypsin and chymotrypsin, secreted by pancreas and which reach the intestine through bloodstream.

13.10 | CATALYSTS IN INDUSTRY

The presence of a catalyst is very useful in many industrial processes. The use of catalyst increases the rate of reaction and in many cases makes it proceed at lower temperature and pressure conditions, thus reducing the cost of production. A few examples of industrial applications of catalysts are given in the Table 13.3.

Table 13.3 Catalysts used in some industrially important processes

S. No.	Process	Catalyst
1.	Haber's process of manufacturing ammonia $N_2 + 3H_2 \rightarrow 2NH_3$	Finely divided Fe and Mo as promoter
2.	Manufacture of vegetable ghee by hydrogenation of vegetable oil	Ni
3.	Contact process of manufacturing sulphuric acid	Pt
4.	Manufacturing methyl alcohol from water gas $CO + 2H_2 \rightarrow CH_3OH$	ZnO and Cr_2O_3 as promoters
5.	Acetic acid from acetaldehyde $2CH_3CHO + O_2 \rightarrow 2CH_3COOH$	V_2O_5
6.	Manufacturing chlorine by Deacon's process $4HCl + O_2 \rightarrow 2H_2O + 2Cl_2$	$CuCl_2$
7.	Ostwald's process of manufacturing nitric acid $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$ $2NO + O_2 \rightarrow 2NO_2$ $4NO_2 + 2H_2O + O_2 \rightarrow 4HNO_3$	Platinized asbestos
8.	Manufacturing hydrogen by Bosch's process $\underbrace{CO + H_2}_{\text{Water gas}} + H_2O \rightarrow CO_2 + 2H_2$	Fe_3O_4 and Cr_2O_3 as promoters

Solved Example 13-24

Name the process catalyzed by the following catalysts: **(a)** $[RhCl(PPh_3)_2]$; **(b)** $TiCl_4 + Al(C_2H_5)_3$; **(c)** Ru and **(d)** nickel.

Solution

(a) $[RhCl(PPh_3)_2]$: hydrogenation.

(b) $TiCl_4 + Al(C_2H_5)_3$: polymerization

(c) Ru: Haber–Bosch process.

(d) Nickel: hydrogenation

Solved Example 13-25

Which catalyst is involved in thermite process?

Solution

In case of thermite process, which is highly exothermic no external catalyst is required.

13.11 | COLLOIDS

The word ***colloid***, a name derived from the Greek *kolla*, meaning "glue," and was coined by the English scientist Thomas Graham in 1861. It means a dispersion in which the dispersed particles are larger than the solute ions or molecules of a true solution and smaller than the particles of a mechanical suspension. The size of colloidal particles ranges from a lower limit of about 1 nm (10^{-7} cm) to an upper limit of about 100 nm (10^{-5} cm). Another important characteristic of colloids is that the particles have relatively huge surface areas. The diameter of the colloidal particle is about 1000 times that of the solute particle. Because the volumes of spheres are proportional to the cubes of their diameters, we can calculate that the volume of a colloidal particle can be up to a billion ($10^3 \times 10^3 \times 10^3 = 10^9$) times greater than that of a solution particle.

Note: The surface area is increased ten-fold when a 1 cm cube is divided into 1000 cubes with sides of 0.1 cm. When a 1 cm cube is divided into colloidal-size cubes measuring 10^{-6} cm, the combined surface area of all the particles becomes a million times greater than that of the original cube.

Graham referred the colloid to substances that were unable to diffuse through semi-permeable membranes – because the particle size was too large. For example, milk is mainly water-based and contains water-soluble calcium compounds. A part of it is also made up of fat-based water-insoluble compounds. The fat particles remain dispersed in the milk and milk is hence a colloid. The water-based phase of milk is known as **dispersal medium** and the fat-based phase is known as **dispersed medium**.

A **colloid** can thus be defined as a heterogeneous system in which one substance is dispersed (dispersed phase) as very fine particles in another substance called the dispersion medium.

The same substance may exist as colloid under certain condition and as crystalloids under certain other conditions. When the size of the solute particle lies between 1 nm and 100 nm, it behaves as a colloid. Hence, we can say that colloid is not a substance but a state of the substance which is dependent on the size of the particle. A colloidal state is intermediate between a **true solution** and a **suspension**. For example, sulphur is a substance, but colloidal sulphur is sulphur dispersed in water, in which sulphur atoms combine to form multimolecules.

The differences between a colloidal dispersion and a true solution are tabulated in Table 13.4.

Table 13.4 Difference between colloid in true solution and colloidal solutions

Property	True solution	Colloidal solutions
Size of the particles	< 1 nm	1–100 nm
Nature	Homogeneous	Heterogeneous

(*Continued*)

Table 13.4 (Continued)

Property	True solution	Colloidal solutions
Filterability (diffusion through parchment paper)	Particles of true solution diffuse rapidly through filter paper as well as parchment paper.	Colloidal particles pass through filter paper but not through parchment paper.
Visibility	Particles of true solution are not visible to naked eye.	Colloidal particles are not seen to naked eye, but can be studied through ultramicroscope.
Tyndall effect	True solution does not show Tyndall effect.	Colloids shows Tyndall effect.
Appearance	Transparent	Translucent

Types of Colloids

A colloid is a broad category of mixtures in which one phase is suspended in the other. They may be classified based on the physical state of particles in the dispersed phase and dispersion medium (Table 13.5); the nature of interactions between them; and size of particles of the dispersed phase.

Table 13.5 Types of colloid dispersion

Dispersed phase	Dispersion medium	Name	Example
Gas	Gas	–[a]	–
Liquid	Gas	Liquid aerosol	Fog, perfume spray
Solid	Gas	Solid aerosol	Smoke, dust
Gas	Liquid	Foam	Fire extinguisher foam, shaving foam
Liquid	Liquid	Emulsion	Milk, mayonnaise
Solid	Liquid	Sol, paste	Toothpaste, crystallization
Gas	Solid	Solid foam	Expanded polystyrene, cushion foam
Liquid	Solid	Solid emulsion (gel)	Opal, pearl
Solid	Solid	Solid suspension (sol)	Pigmented plastics

[a] *A gas-in-gas system is not a colloid, it is a mixture.*

Colloids can be classified based on a number of criteria such as nature of dispersion medium, type of interaction between dispersion medium and dispersed phase and molecules of dispersed phase.

I. Based on the dispersion medium:

1. A gas suspended in a liquid or a solid is called **foam**.
2. A liquid dispersed in a different liquid is called an **emulsion**.
3. A solid or liquid suspended in a gas is known as **aerosol**.
4. A solid suspended in a liquid is called a **sol**; when the dispersion medium is water, it may be termed as **hydrosol**.

Note: Like milk, ice cream is also a colloid. It is both an emulsion and partially solidified foam. The solid part is a network of globules of emulsified fat and ice crystals. Air beaten into it forms solidified foam and imparts creamy texture to the ice cream.

II. Based on the nature of interactions between the dispersed phase and dispersion medium:

1. **Lyophilic colloids:** These are colloidal solutions in which the dispersed particles have strong affinity for the dispersion medium.
   - (a) In these systems, the colloidal particles pass readily into the dispersion medium by simple mixing
   - (b) If the dispersed phase is isolated by removal of dispersion medium, it is possible to reconstitute the colloidal solution simply by adding the dispersion medium again. They are, therefore, called **reversible sols**. In case of lyophilic colloids if we remove the dispersion medium completely by vaporization , only the colloidal particles or the dispersed phase will remain. These colloidal particles have a very strong interaction with the dispersion

medium. (It is a characteristic of lyophilic colloids that they form very stable colloid solutions.) Thus even when these colloid particles are added back to the dispersion medium, they readily form colloidal solutions.

- **(c)** If the dispersion medium is water, the colloidal solution is called **hydrophilic sol**.
- **(d)** Some examples are starch, gum, gelatin, etc., dissolved in a suitable solvent.

2. **Lyophobic colloids:** These are colloidal solutions in which the dispersed phase has a weak interaction with the dispersion medium are called **lyophobic sols**.
   - **(a)** The dispersed phase does not like to get dissolved in dispersion medium so these are not formed by simple mixing of dispersed phase in dispersion medium and require special methods for their preparation.
   - **(b)** These colloidal systems can be easily precipitated or coagulated by heating, shaking or addition of small amount of electrolytes.
   - **(c)** The addition of dispersion medium to the precipitated colloidal particles does not reconstitute the colloidal sol again; hence these are called **irreversible sols**. In case of lyophobic colloids, the cohesive or interactive forces are very weak between the colloid particles/dispersed phase and dispersion medium. On removal of the dispersion medium from the colloidal solution, the colloid particles or the dispersed phase is separated. But when the colloidal particles are mixed again with the dispersion medium, they will not form the colloid solution due to further weakening of already weak force of attraction between the dispersed phase and the dispersion medium.
   - **(d)** If the dispersion medium is water, the colloidal solution is called **hydrophobic sol**.
   - **(e)** Some examples are metals in water, metal sulphides in water, etc.

III. Based on the types of molecules in the dispersed phase:
This classification is based on the type of molecules in the dispersed phase and colloidal dimensions.

1. **Multimolecular colloids:** In these colloids, the particles (atoms or small molecules) of the dispersed phase aggregate to form particles of colloidal size (diameter > 1 nm). Some examples are, a sol of sulphur containing S_8 molecules as multimolecular particles, a sol of aggregated As_2S_3 molecules and gold sol in which atoms of gold are condensed to form multimolecular gold particles. Note that the term multimolecular does not refer only to molecules but also includes atoms and ions as aggregating particles.
2. **Macromolecular colloids:** If the individual particles of the dispersed phase have dimensions similar to colloidal size, the dispersion is called macromolecular colloid. The articles of colloidal dimensions include naturally occurring molecules such as proteins, enzymes, cellulose, rubber, etc., and synthetic materials like polystyrene, polyethylene, synthetic rubber, etc. Proteins dissolved in water and rubber dissolved in benzene are examples of macromolecular colloids.
3. **Associated colloids:** In these colloids, the dispersed phase is made up of particles that behave as regular electrolytes at lower concentrations but aggregate at higher concentrations to form particles of colloidal dimension. The aggregated molecules, thus, formed are called **micelles**. On dilution, these aggregates revert back to their original electrolyte state. Two important characteristics of micelle formation are **Kraft temperature** (T_k), which is the temperature above which micelle formation takes place and **critical micelle concentration** (CMC), which is the concentration above which micelle formation takes place. The most common example of associated colloids are solutions of soap or detergent in water.

Mechanism of Micelle Formation

This is observed in substances such as soaps and detergents when dissolved in water. Soaps are sodium or potassium salts of long-chain carboxylic acids that can be represented as $RCOO^-Na^+/K^+$, where R is a long-chain alkyl group, such (stearate, palmitate, etc. When dissolved in water, soap molecules break up into $RCOO^-$ and Na^+ or K^+ ions. The $RCOO^-$ ion contains both a hydrophilic(negatively charged carboxylate group) and a hydrophobic (long hydrocarbon chain) group. The hydrophilic carboxylate group is soluble in water while hydrocarbon group is soluble in oils and greases. In dilute solutions, $RCOO^-$ ions are oriented at the surface of water with their COO^- group in water and hydrocarbon chain away from it [Fig. 13.12(a)]. Except in very dilute solutions, soaps exists as **micelles**. Soap micelles are usually spherical clusters of carboxylate anions that are dispersed throughout the aqueous phase. The carboxylate anions are packed together with their negatively charged (and thus, *polar*) carboxylate groups at the surface and with their non-polar hydrocarbon chains on the interior. The sodium ions are scattered throughout the aqueous phase as individual solvated ions [Fig. 13.12(b)].

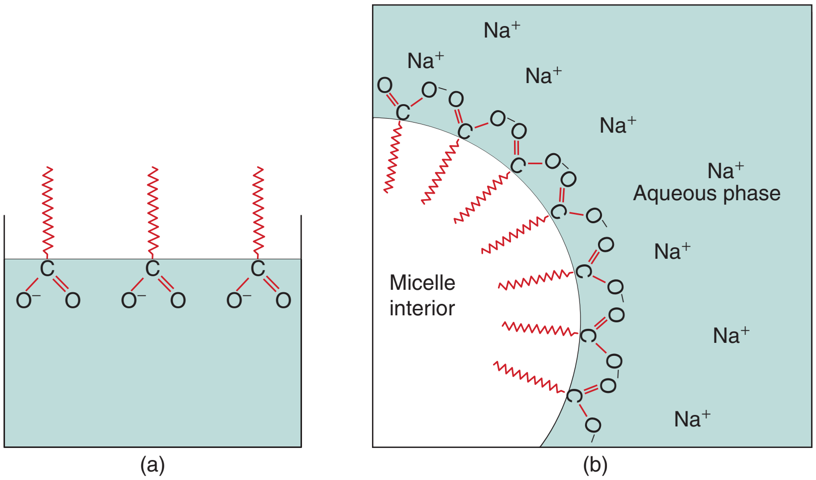


Figure 13.12 (a) $RCOO^-$ ions in dilute soap solution. (b) A portion of a soap micelle showing its interface with the polar dispersing medium.

Micelle formation accounts for the fact that soaps dissolve in water. The non-polar (alkyl chains of the soap remain in a non-polar environment – in the interior of the micelle. The polar carboxylate groups are exposed to a polar environment – that of the aqueous phase. Since the surfaces of the micelles are negatively charged, individual micelles repel each other and remain dispersed throughout the aqueous phase. Synthetic detergents function in the same way as soaps; they have long non-polar alkane chains with polar groups at the end. The polar groups of most synthetic detergents are sodium sulphonates or sodium sulphates.

Solved Example 13-26

Classify the following as multimolecular, macromolecular and associated colloids: **(a)** sulphur, **(b)** rubber in benzene, **(c)** soap in water and **(d)** gold sol.

Solution

(a) Sulphur – multimolecular colloids
(b) Rubber in benzene – macromolecular colloids
(c) Soap in water – associated colloid
(d) Gold sol – multimolecular colloid

Solved Example 13-27

Why is a colloidal sol stable?

Solution

Hydrophobic sols are stabilized by the presence of like charges on colloidal particles. Due to the presence of like charges, colloidal particles repel each other and move away from each other; and thus do not coalesce to form bigger aggregates. However, the coagulation begins immediately on the removal of the charge. Stability of lyophilic colloids is for two reasons. Their particles possess a charge, and in addition, they are heavily solvated and the solvent layer surrounding them prevents them to come into intimate contact with each other. Hence their coagulation is prevented. For example, when sodium chloride is added to a gold sol, it gets precipitated. However, when sodium chloride is added to a colloidal solution of gelatin, its particles are not precipitated. This is because the water layer around gelatin particles does not allow Na^+ ions to penetrate and destroy the charge on gelatin particles.

Solved Example 13-28

Colloid is not a substance but a state of substance. Justify.

Solution

The same substance may exist as colloid under certain condition and as crystalloids under certain other conditions. When the size of the solute particle lies between 1 nm and 100 nm, it behaves as a colloid. Hence, we can say that colloid is not a substance but a state of the substance which is dependent on the size of the particle. A colloidal state is intermediate between a true solution and a suspension. For example, sulphur is a substance, but colloidal sulphur is sulphur dispersed in water, in which sulphur atoms combine to form multimolecules.

13.12 | PREPARATION OF COLLOIDS

The methods for preparation of colloids depend on the nature of colloidal particles constituting the dispersed phase.

1. Some colloids, such as **lyophilic colloids** can be formed by dissolving the colloidal particles in dispersion medium. For examples, sols of gum, starch, gelatin, may be prepared in this manner. Solutions of colloidal electrolytes such as soap and dyes can also be prepared by simple dissolution of the particles in dispersion medium.
2. Substances that do not disperse easily in dispersion medium, that is, **lyophobic sols** need special methods for formation of their colloidal solutions.

Lyophobic sols can be prepared by either by breaking down the bulk particles to finer colloidal size particles (**dispersion method**) or aggregating the molecular dimension particles to form aggregates of colloidal size (**condensation method**). A third substance, called stabilizer, is sometimes added to stabilize the lyophobic sol.

Dispersion Methods

1. **Mechanical dispersion:** This involves mechanical grinding of the particles to be dispersed to almost colloidal dimensions and then mixing them with dispersion medium to obtain a suspension. The suspension is then run through a colloid mill which consists of two metal discs held some distance apart and capable of revolving at a high speed in opposite directions. This process grinds the particles to colloidal size and these get dispersed in the solution. A stabilizer can be added for stabilization, For example, a colloidal solution of graphite and printing ink is made using this method and tannin is added as the stabilizer.
2. **Ultrasonic dispersion:** In this method, ultrasonic waves of high frequency are used to disperse the particles to colloidal state. For example, mercury, sulphur and sulphides of metals can be dispersed using this method.
3. **Electrical disintegration or Bredig's arc method:** This method is used for preparation of colloids of metals such as gold, silver, copper, platinum, etc. In this method, the metal that needs to be dispersed is made into two electrodes and dipped in the dispersion medium. An electric arc is struck between the electrodes and the heat generated by the arc vaporizes the metal. These vapors condense when they come in contact with dispersion medium cooled in an ice-bath and form colloidal particles that get dispersed to form a sol (Fig. 13.13).
4. **Peptization:** This is a process wherein a freshly generated precipitate is converted into a colloidal sol by shaking it in dispersion medium in the presence of an electrolyte which is called **peptizing agent**. For example, a dark red colored sol of $Fe(OH)_3$ is obtained when freshly prepared precipitate is treated with small amount of $FeCl_3$ solution. The precipitate adsorbs the Fe^{3+} ions from the electrolyte on its surface and develops positive and negative charges. This causes the precipitate to disintegrate into particles of colloidal size. In certain cases, the dispersion medium may act as peptizing agent causing the precipitate to disperse in it. For example, ethanol used as dispersion medium causes dispersion of cellulose nitrate.

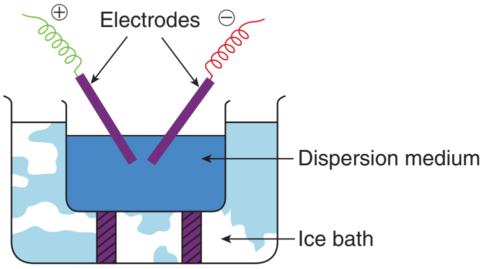


Figure 13.13 Electrical disintegration or Bredig's arc method.

Condensation Methods

1. **Physical methods:** These methods include techniques like solvent exchange (i.e., taking the solution in one solvent and pouring it into the other), excessive cooling or condensation of vapors. Examples of each type are:
   - **(a)** A colloidal solution of sulphur or phosphorus is obtained by pouring the alcoholic solution of these elements into water.
   - **(b)** When a mixture of ice and chloroform undergoes sudden cooling to very low temperatures, ice crystal are obtained as colloidal dispersion in chloroform.
   - **(c)** Metal sols of metals with low melting points can be prepared by passing and collecting their vapor in cold water.
2. **Chemical methods:** In this method, the colloidal molecules or aggregates are formed by means of chemical reactions such as decomposition, hydrolysis, oxidation or reduction. Some examples of each type are:

$$\mathrm{As_2O_3 + 3H_2S \xrightarrow{\text{Double decomposition}} \underset{\text{Yellow sol}}{As_2S_3} + 3H_2O}$$

$$\mathrm{FeCl_3 + 3H_2O \xrightarrow{\text{Hydrolysis}} Fe(OH)_3 + 3HCl}$$

$$\mathrm{SO_2 + 2H_2S \xrightarrow{\text{Oxidation}} \underset{\text{(Sol)}}{3S} + 3H_2O}$$

$$\mathrm{2AuCl_3 + 3SnCl_2 \xrightarrow{\text{Reduction}} 3SnCl_4 + 2Au}$$

Solved Example 13-29

How are the following sols in water prepared: **(a)** Sulphur and **(b)** ferric hydroxide?

Solution

(a) Sol of sulphur is prepared when H_2S gas is bubbled through solution of an oxidizing agent such as bromine H_2O or nitric acid, etc.

$$\mathrm{H_2S + 2HNO_3 \rightarrow 2H_2O + 2NO_2 + S}$$

(b) $Fe(OH)_3$ sols are obtained by hydrolysis of $FeCl_3$.

$$\mathrm{FeCl_3 + 3H_2O \rightarrow Fe(OH)_3 + 3HCl}$$

13.13 | PURIFICATION OF COLLOIDAL SOLUTIONS

The colloidal sols prepared generally contain some impurities which depend on the process used for the preparation of colloids. These impurities are generally electrolytes that destabilize the colloid causing it to coagulate. In the case of colloidal solution being used as medicines, these impurities may be harmful. It is important to purify the colloidal solution to reduce the level of these impurities to minimum. Some important methods used for purification of solids are discussed as follows.

1. **Dialysis:** Thomas Graham found that a parchment membrane would allow the passage of true solutions but would prevent the passage of colloidal dispersions. Dissolved solutes can be removed from colloidal dispersions through the use of such a membrane by a process called **dialysis**. The membrane itself is called a **dialyzing membrane**. Artificial membranes are made from materials such as parchment paper or certain kinds of cellophane. Dialysis can be demonstrated by putting a colloidal starch dispersion and some copper(II) sulphate solution in a parchment paper bag and suspending it in running water. In a few hours, the blue color of the copper(II) sulphate has disappeared, and only the starch dispersion remains in the bag (Fig. 13.14).

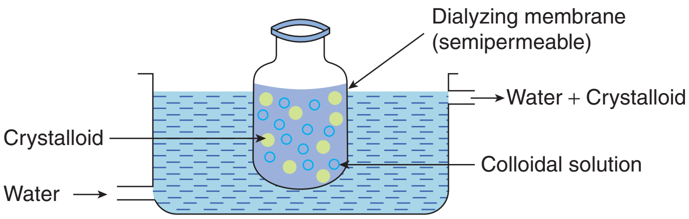


Figure 13.14 Demonstration of dialysis.

2. **Electrodialysis:** The process of dialysis is generally slow and can be made faster by applying an electric field. The process is then called electrodialysis and is applicable to impure colloidal solutions that have ions (electrolyte) as impurities. In this process, the two electrodes are placed in a compartment containing water and the colloidal solution placed in a bag of suitable membrane. When current is passed, the ions are attracted by the oppositely charged electrodes and removed (Fig. 13.15).
3. **Ultrafiltration:** This process involves removal of impurities from colloidal solutions by filtering through specially prepared filter papers. These filter papers are prepared in a manner that they are permeable to all substances apart from the colloidal particles. The ordinary filter papers cannot be used for this process because their pores are very large and permit passage of colloidal particles. So they are impregnated with collodion solution (4% solution of cellulose nitrate in alcohol + ether), hardened using formaldehyde, dried and then used for ultrafiltration. Filter papers of desired pore size can be obtained by using solutions of different concentration of collodion. The process of ultrafiltration is also slow and can be made faster by applying pressure.

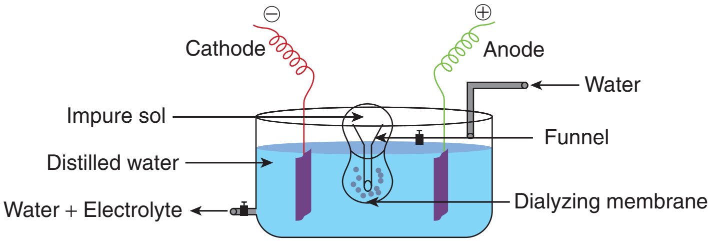


Figure 13.15 Electrodialysis.

Solved Example 13-30

What happens when persistent dialysis of a colloidal solution is carried out?

Solution

The stability of colloidal sols is due to the presence of a small amount of electrolyte. If the electrolyte is completely removed by persistent dialysis, the particles left will get coagulated.

Solved Example 13-31

Frequently, preparation of a colloid such as a protein can be made more stable if the colloid is dialyzed. Why is this so?

Solution

This is because dialysis helps in removing undesirable ions from a colloidal preparation, which tend to destabilize the colloid.

Solved Example 13-32

Which method is employed in separation of plasma proteins?

Solution

Plasma proteins can be divided into various fractions using electrodialysis.

13.14 | PROPERTIES OF COLLOIDAL SOLUTIONS

1. Colloidal solutions are heterogeneous in nature because they are made of two different phases, that is, the dispersed phase and dispersion medium.
2. Particles with diameter less than 200 μm cannot be seen by naked eye. Since the upper size range of colloidal particles is 100 nm, these are not visible to the naked eye. The size and shape of colloidal particles can be determined using scanning electron microscope (SEM); transmission electron microscope (TEM) and scanning transmission electron microscope (STEM).

3. The surface area of particles in colloidal state is considerably larger than the area of the substance as a solid mass. This increased surface area is responsible for the tendency of colloids for adsorption.
4. Surface tension and viscosity of lyophobic sols is the same as that for pure solvent. However, in lyophilic sols the viscosity is higher than the pure solvent and surface tension is lower.
5. **Colligative properties:** In colloidal solutions, smaller particles (atoms/molecules) aggregate to form bigger particles of colloidal dimension. Hence, the number of particles in colloidal solution is effectively reduced as compared to what it would be in a true solution. We know that the colligative properties of solutions (osmotic pressure, lowering of vapor pressure, boiling point elevation or freezing point depression) depend on number of particle of solute. As a result, in colloidal solutions, the values of colligative properties is of lower order as compared to true solutions of same concentration.
6. **Brownian movement:** In 1827, while observing a strongly illuminated aqueous suspension of pollen under a high-powered microscope, Robert Brown (1773–1858) noted that the pollen grains appeared to have a trembling, erratic motion. He later determined that this erratic motion is not confined to pollen but is the characteristic of colloidal particles in general. This random motion of colloidal particles is called **Brownian movement**. The dispersed particles appear as tiny randomly moving lights because the light is reflected from their surfaces. This motion is due to the continual bombardment of the dispersed particles by the dispersion medium (Fig. 13.16).

   The Brownian movement is observed in all colloidal solutions and is independent of the nature of colloidal particles. It, however, varies with the size of the particles and viscosity of the solution. Smaller particles with lower viscosity show faster movement.

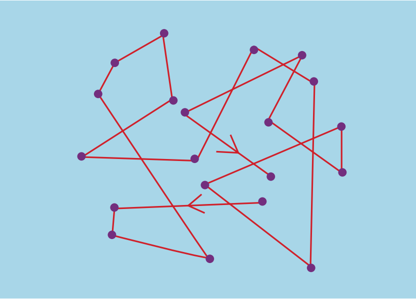


Figure 13.16 Brownian movement.

7. **Tyndall effect:** When an intense beam of light is passed through an aqueous solution of copper nitrate and viewed at an angle, the beam passing through the solution is hardly visible. A beam of light, however, is clearly visible and sharply outlined when it is passed through a colloidal dispersion. This phenomenon is known as the **Tyndall effect**. This effect, like Brownian movement, can be observed in nearly all colloidal dispersions. It occurs because the colloidal particles are large enough to scatter the rays of visible light. The ions or molecules of true solutions are too small to scatter light and therefore do not exhibit a noticeable Tyndall effect.

Note: Tyndall effect is also observed in suspensions but is less prominent than in colloidal solutions. This is due to the large particle size of the suspensions which causes multiple deflections from the surface and thus diffuses the effect.

This phenomenon was first discovered by Faraday and later studied by Tyndall. The colloidal particles absorb the incident light and then scatter it and thus get illuminated. The path of light through the colloidal solution when observed by a microscope appears as a bluish cone that is known as **Tyndall cone**. The scattering of light is a function of the wavelength of the incident light and the angle between incident and scattered light. The conditions necessary for observation of Tyndall effect are: **(a)** The diameter of the particles should be of the order of wavelength of light used and **(b)** the refractive indices of the dispersed phase and the dispersion medium should be vastly different (Fig. 13.17).

Note: Lyophobic colloids have higher refractive index, thus Tyndall effect is more prominent in lyophobic colloids as compared to lyophilic colloids.

Note: A beam of light is visible in a colloidal solution but not in a true solution. The size of particles in the colloid is large enough to scatter the light beam and make it visible.

Some examples of Tyndall effect are as follows:

(a) When a car headlight is shone directly on a blanket of fog or mist, the light is scattered and a blinding effect is observed. However, if yellow or amber fog lights are used, light scattering actually improves visibility in fog. This is because in increasing intensity results in increased scattering, whereas by eliminating shorter wavelengths (violet, indigo and blue) the scattering effect is reduced.

(b) In a cinema hall, during the projection of the film on the screen, the path of light can be seen due to Tyndall effect. The light is scattered by the dust and smoke particles in the air.

(c) Milk has a cloudy appearance due to scattering of visible light by the suspended fat globules.

Positively charged:	$Fe_2O_3 \cdot xH_2O/Fe^{3+}$
Negatively charged:	$Fe_2O_3 \cdot xH_2O/OH^-$ and As_2S_3/S^{2-}

Note: Colloidal particles become electrically charged when they adsorb ions on their surface. Each colloidal particle is surrounded by an electrical double-layer.

Once the colloidal particle has acquired positive or negative charge, it has a tendency to attract the oppositely charged ions from the solution to form a layer around it. This results in a combination of two layers of charges around the colloidal particle known as **Helmholtz electrical double layer**. The first layer of charges is firmly held to the colloidal surface while the second layer of charge is diffused. A potential difference is set up between the two layers because of the fixed and diffused charges of opposite signs and is known as **electrokinetic potential** or **zeta potential**.

(b) Electrons are captured during the electrode dispersion of metals in Bredig's arc method.

(c) Dissociation of ions from surface of colloids. For example, when soap is dissolved in water, it dissociates to form ions ($RCOO^-$ and Na^+/K^+). The positive ions pass into the solution and carboxylate ions form negatively charged colloidal particles (micelles).

(d) The presence of acidic and basic groups in the colloidal particles, such as proteins, leads to formation of positively and negatively charged solutions in acidic and basic medium, respectively.

10. Electrophoresis: It is the phenomenon of migration of colloidal particles towards oppositely charged electrodes under the influence of applied electrical potential. The negatively charged particles move towards anode and positively charged particles move towards cathode. This property thus helps us to determine the nature of charge on the colloidal particles. The phenomenon can be demonstrated experimentally by taking the colloidal solution of $Fe(OH)_3$ in a U-tube and dipping two platinum electrodes into the two arms (Fig. 13.18). The intensity of color of solutions in each arm is the same. However, when current is passed for an interval of time, the intensity of the color increases near the negative electrode. This shows movement of colloidal particles towards negative electrode and hence its positive nature.

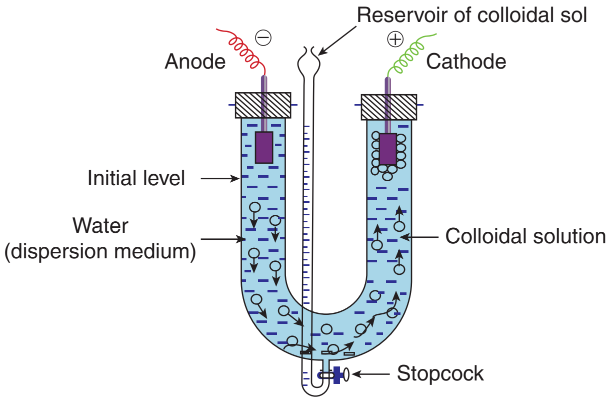


Figure 13.18 Electrophoresis.

If the movement of colloidal particles under the effect of electric field is prevented by some method (such as use of porous diaphragm), it is found that the dispersion medium begins to move towards the electrodes. This migration of dispersion medium (solvent) under the effect of electric field is known as **electro-osmosis**. We can also determine the nature of charge on colloidal particles from the process of electro-osmosis.

Solved Example 13-33

A colloidal solution of AgI is prepared by two different methods as shown in the Fig. 13.19:

(a) What is the charge on AgI colloidal particles in the two tubes (A) and (B)?

(b) Give reason for the origin of charge in the figure.

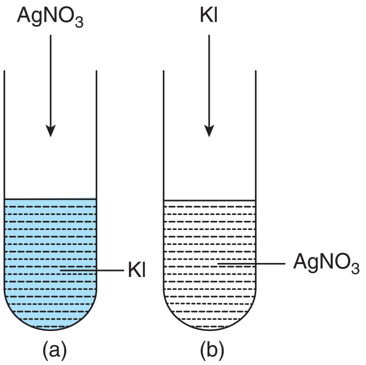


Figure 13.19

Solution

(a) The two tubes (A) and (B) contain
(A) negatively charged sol – AgI:I^- and (B) positively charged sol – AgI:Ag^+

(b) When $AgNO_3$ is added to KI, AgI is precipitated which adsorbs I^- ions from KI and thus forms negatively charged sol AgI:I^-. When KI is added to $AgNO_3$ solution, positive sol is formed due to adsorption of Ag^+ ions from $AgNO_3$.

Solved Example 13-34

Why is Tyndall effect not shown by true solutions?

Solution

Tyndall effect is not shown by true solutions because the ions or solute molecules are of such minute sizes that they cannot reflect light. This effect can therefore be used to distinguish between a true solution and a colloidal solution.

Solved Example 13-35

What is the charge of colloidal particles in **(a)** soap sol; **(b)** gold sol; **(c)** haemoglobin; **(d)** starch; **(e)** prussian blue dye; **(f)** rain water?

Solution

(a) Colloidal particles of soap solution in water are negatively charged.

(b) All metallic sols are positively charged sol, for example, gold sol.

(c) Metallic hydroxide sols like haemoglobin are positively charged.

(d) Starch, gum are negatively charged sols.

(e) Basic dyes like Prussian blue are positively charged.

(f) Rainwater contains impurities, which bear a negative charge. When raindrops are broken in a vertical blast on striking against each other, they develop a negative charge, if the concentration of impurities is more than $5 \times 10^{-5}\%$.

13.15 | COAGULATION OR PRECIPITATION AND HARDY–SCHULZE RULE

The stability of colloidal solutions is due to presence of similar and equal charges on the particles that prevents the particles from coalescing. If this charge is removed or neutralized in some manner, the particles approach each other and aggregate to form a precipitate. The colloid is said to be *broken* when the dispersion medium no longer suspends the dispersed phase. **Coagulation** is a process which involves coming together of colloidal particles so as to change into large-sized particles which ultimately settle as a precipitate or float on the surface. The various ways in which the colloidal particles may be coagulated are listed discussed below for lyophobic and lyophilic sols.

Coagulation of Lyophobic Sols

It can be carried out by using the following methods.

1. **By dialysis:** We have learnt that dialysis may be used for purification of colloidal solutions to remove the presence of ions. However, if by prolonged dialysis all the ions present in the colloidal solution are removed, the colloidal particles settle as a precipitate.

2. **By mixing oppositely charged colloidal solutions:** When two oppositely charged sols are mixed in equal proportions, their charges get neutralized and coagulation takes place. This process is known as **mutual coagulation**. For example, when negatively charged arsenious sulphide sol is mixed with positively charged ferric hydroxide sol, both are precipitated.

3. **By electrophoresis:** In this process, the charged particles moving towards oppositely charged electrodes may get discharged and precipitate out.
4. **By boiling:** When the colloidal solution is boiled, the number of collisions between the dispersion medium and the charged layer on the colloidal surface increases. This reduces the charge on the particles leading them to coagulate.
5. **By addition of electrolytes:** The addition of an electrolyte causes precipitation of sols. The addition of electrolyte itself is not responsible for the coagulation. Instead the presence of ions which carry a charge opposite to that on the colloidal particles is responsible for its precipitation. This is because when these ions are added in excess; the oppositely charged ions present on the surface of the colloidal particles are neutralized, leading to coagulation.

The minimum concentration of electrolyte (in millimoles) required to bring about the coagulation of one liter of colloidal solution in two hours is called its **coagulation** or **flocculation value**. The reciprocal of coagulation value is the coagulating power of the coagulating or flocculating electrolyte. Comparison of coagulation power of different electrolytes has shown that greater the valence of the flocculating ion added, greater is its power to cause precipitation; this is known as **Hardy–Schulze rule**. Thus, the coagulating powers of anions follow the order: $PO_4^{3-} > SO_4^{2-} > Cl^-$. Similarly, coagulating power of the cations follow the order: $Al^{3+} \gg Mg^{2+} > Na^+$.

Coagulation of Lyophilic Sols

In addition to the presence of charged particles, the stability of lyophilic sols also arises due to solvation of particles. Thus for coagulating a lyophilic sol both these stabilizing factors need to be removed. Addition of solvents such as acetone and alcohol dehydrate the solvated ions of the dispersed phase and addition of small amounts of electrolyte then causes the colloidal particles to coagulate.

Hardy–Schulze Rule

The coagulation capacity of different electrolytes is different. It depends on the valence of the active ion called flocculating ion, which is the ion carrying charge opposite to the charge on the colloidal particles. According to Hardy–Schulze rule, greater the valency of the active ion or flocculating ion, greater will be its coagulating power. Thus, Hardy–Schulze law states:

1. The ions carrying the charge opposite to that of sol particles are effective in causing coagulation of the sol.
2. Coagulating power of an electrolyte is directly proportional to the valency of the active ions (ions causing coagulation). For example, to coagulate negative sol of As_2S_3, the coagulation power of different cations has been found to decrease in the order as, $Al^{3+} > Mg^{2+} > Na^+$. Similarly, to coagulate a positive sol such as $Fe(OH)_3$, the coagulating power of different anions has been found to decrease in the order: $[Fe(CN)_6]^{4-} > PO_4^{3-} > SO_4^{2-} > Cl^-$.

Drawback: Hardy–Schulze law takes into consideration only the charge carried by an ion, not its size. The smaller the size of an ion, the more will be its polarizing power. Thus, Hardy–Schulze law can be modified in terms of the polarizing power of the flocculating ion. Thus, the modified Hardy–Schulze law can be stated as “the greater the polarizing power of the flocculating ion added, the greater is its power to cause precipitation”.

Solved Example 13-36

Which one of the following electrolytes is most effective for the coagulation of $Fe(OH)_3$ sol and why: NaCl, Na_2SO_4, Na_3PO_4?

Solution

To coagulate a positive sol such as $Fe(OH)_3$, the coagulating power of different anions has been found to decrease in the order: $PO_4^{3-} > SO_4^{2-} > Cl^-$. This is because the coagulating power of an electrolyte is directly proportional to the valence of the active ions (ions causing coagulation).

Solved Example 13-37

Which of the following will have a lower coagulating value in coagulating $Fe(OH)_3$ sol and why: Na_2SO_4 or $K_3[Fe(CN)_6]$?

Solution

SO_4^{2-} has lower coagulating value than $Fe(CN)_6^{4-}$ because according to Hardy–Schulze rule, the more is the charge on the anion, the more is its coagulating value or in other words, less is the charge on the anion, lower is its coagulating value.

Solved Example 13-38

Compare the coagulating power of $AlCl_3$ with that of NaCl. Given that their coagulation values are 0.093 and 52, respectively.

Solution

Coagulating power is inversely proportional to the coagulating value. So,

$$\frac{\text{Coagulating power of } AlCl_3}{\text{Coagulating power of NaCl}} = \frac{\text{Coagulation value of NaCl}}{\text{Coagulation value of } AlCl_3}$$

$$= \frac{52}{0.093} = 559$$

which means that $AlCl_3$ has 559 times greater coagulation power than NaCl.

13.16 | PROTECTION OF COLLOIDS

Lyophilic sols show greater stability than lyophobic sols due to salvation of particles by the dispersion medium. These sols can be added to lyophobic sols to protect them from coagulating in presence of added electrolyte. The lyophilic sol particles form a protective layer around the lyophobic colloidal particles thus protecting them from electrolytes. Such lyophilic colloids are known as **protective colloids**. Some examples include addition of gelatin in preparation of ice cream and addition of gum Arabic in India ink.

The protective power of lyophilic solution is expressed in terms of gold number. **Gold number** is the number of milligrams of the protective colloid that will just prevent the coagulation of 10 ml of a gold sol on the addition of 1 ml of 10% sodium chloride solution. The smaller the value of gold number, the greater is the protecting power of the protective collloid. Therefore, the reciprocal of gold number is a measure of the protective power of a colloid. For example, Gelatin with lowest gold number (0.005) is considered the best protective colloid. The gold number of some of the protective colloids are listed in Table 13.6.

Table 13.6 Gold number of some protective colloids

Protective colloid	Gold number
Gelatin	0.005–0.01
Casseum	0.01–0.02
Haemoglobin	0.03–0.07
Albumin	0.1–0.2
Gum Arabic	0.15–0.25
Starch	20–25

Solved Example 13-39

The coagulation of 100 mL of a colloidal solution of gold is completely prevented by adding 0.08 g of starch to it before adding 10 mL of 10% NaCl solution. What is the gold number of starch?

Solution

Amount of starch adsorbed (in 100 mL) = 0.08 × 1000 = 80 mg

Gold number = 80 × 10% (NaCl) = 80 × 10/100 = 8.

Solved Example 13-40

Gold number of gum Arabic is 0.15. What is the amount of gum Arabic required to protect 100 mL of red gold sol from coagulation by 10 mL of 10% NaCl solution?

Solution

(d) Gold number is the minimum amount of lyophilic colloid in milligrams which prevents the coagulation of 10 mL gold sol against 1 mL of 10% NaCl. Therefore, 1.5 mg will be used.

Solved Example 13-41

How can lyophobic sols be protected by the addition of lyophilic sols?

Solution

It is known that lyophobic sols are unstable. A lyophobic sol may be protected by the addition of a lyophilic sol. It has been observed that lyophilic sols protect a lyophobic sol by preventing it from coagulating in the presence of an electrolyte. A possible reason might be that the lyophilic colloidal particles form a protective layer around the lyophobic particles.

13.17 | EMULSIONS

An emulsion is prepared by shaking strongly the mixture of the two liquids or by passing the mixture through a colloid mill known as the homogenizer. The emulsions thus prepared from pure liquids are usually not stable and the two liquids separate out on standing. To get a stable emulsion, small quantities of certain other substances are added during preparation. The substances thus added to stabilize the emulsions are called emulsifiers or emulsifying agents. An emulsifier (also known as an emulgent) stabilizes an emulsion by increasing its kinetic stability. The substances commonly used as emulsifying agents are soaps of various kinds, long-chain sulphonic acids or lyophilic colloids such as proteins, gum, and agar.

Generally, one of the liquid dispersed is water and based on that we can have two types of emulsions (Fig. 13.20):

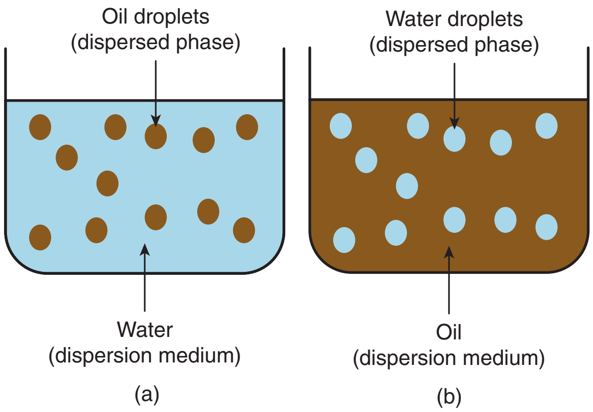


Figure 13.20 Types of emulsions.

1. **Oil-in-water (o/w):** Oil droplets dispersed in water. Examples are milk and vanishing cream. Most oil-in-water emulsions have a creamy texture.
2. **Water-in-oil (w/o):** Water droplets dispersed in oil. Examples of water in oil emulsions are butter, cold cream and cod liver oil. Most water-in-oil emulsions are greasy.

The **tests for emulsion type** (w/o or o/w emulsions) are as follows:

1. **Dilution test:** Based on the solubility of external phase of emulsion, o/w emulsion can be diluted with water and w/o emulsion can be diluted with oil (Fig. 13.21).
2. **Conductivity test:** Water is a good conductor of electricity, whereas oil is non-conductor. Therefore, continuous phase of water runs electricity more than continuous phase of oil. The bulb glows with o/w emulsion, but does not glow with w/o emulsion (Fig. 13.22).
3. **Dye-solubility test:** Water-soluble dye will dissolve in the aqueous phase.

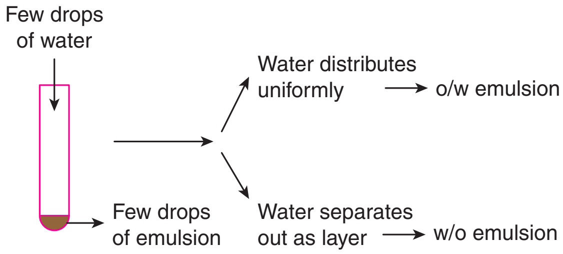


Figure 13.21 Dilution test.

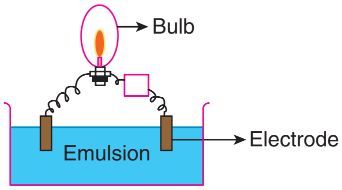


Figure 13.22 Conductivity test.

Emulsification and De-Emulsification

Emulsions of oil-in-water type are unstable and substances called **emulsifying agents** or **emulsifiers** are added during the preparation of the emulsions to stabilize them. Milk is an unusual emulsion that is stable because it contains the naturally occurring protein called casein as emulsifier. Molecules of the emulsifying agent stabilize the colloid by adsorbing to the interface separating the minute particles of oil dispersed in water–oil dispersion. An emulsifier facilitates the dispersion of one liquid into another. Oil particles surrounded by sheath of emulsifier are able to overcome the usual repulsions experienced between oil and water medium and can stay dispersed in the dispersion medium for a longer period of time. Commonly used emulsifying agents for oil-in-water dispersions are soaps, proteins, gums, etc. and for water-in-oil dispersions are long-chain alcohols, metal salts of fatty acids, etc.

Note: Paints are emulsions that consist of pigments bound in synthetic resins such as urethane, which forms an emulsion in water. The water evaporates during the drying of paint.

Emulsions can be broken into constituting particles by heating, freezing, mechanical methods and centrifuging. The process of decomposition of an emulsion into its constituent liquids is called **demulsification**. Examples of demulsifiers are surfactants, ethylene oxide, etc. The emulsions can be diluted by addition of dispersion medium; however, additional dispersed liquid when added forms a separate layer. These also show mechanical properties of colloidal solutions such as Brownian motion and Tyndall effect. The oil droplets in emulsions are generally negatively charged, so emulsions can also be precipitated by addition of electrolytes.

Solved Example 13-42

The conductance of an emulsion increases on adding common salt. What type of emulsion is this?

Solution

This is oil-in-water type emulsion. Adding an electrolyte such as salt to water will increase the electrical conductivity of the aqueous solution and conversely the electrical stability/resistivity of such an aqueous solution will decrease.

Solved Example 13-43

Why do oil particles remain dispersed in the dispersion medium for a longer period of time?

Solution

Oil particles remain dispersed in the dispersion medium for a longer period of time because of emulsifying agent (e.g., proteins, gums) which imparts stability to it by forming interfacial film between the suspended particles and the medium.

13.18 | ROLE OF COLLOIDS IN NATURAL PHENOMENA AND IN INDUSTRY

Some interesting examples of colloids around us are listed as follows:

1. **Colloids in nature:** Many natural phenomena and occurrences are examples of colloids. These include:
    (a) **Blue color of sky:** The brilliant blue color of the sky is due to scattering of light (Tyndall effect) by the dust and water particles that are dispersed in the atmosphere. Similarly, sea water appears blue due to scattering of light by the colloidal impurities present in sea water. The color appears blue because of the scattering of the blue or shorter wavelength of light.

(b) **Color of sunset and sunrise:** The orange or red color of sunset results due to scattering of light by the dust and smoke particles in the atmosphere. These scatter the light of longer wavelength, that is, yellow, orange and red and block light of shorter wavelength, that is, violet, indigo, blue and green. The orange color of sunset is not observed during the day because when the sun is higher, the path that the light has to travel through the atmosphere is much shorter, thus there are fewer dust particles to scatter it. Sunrise is not usually as red as sunset because larger dust particles present in hot air currents during the day settle down in cooler temperature of night. The scattering of light by these particles is to a much lesser extent at the sunrise.

(c) **Comet tail:** Tail of comets can be visualized as Tyndall cone that arises due to the scattering of light by the tiny solid particles left by the comet in its path.

(d) **Fog, mist or rain:** The air in the atmosphere contains many suspended impurities in form of dust and other particulate matter. When the air is cooled, the moisture in the air condenses on the particulate matter and forms droplets of water. These droplets are colloidal in nature and float as mist or fog. Droplets of water are also present in clouds and when they condense and grow bigger in size, they pour down as rain. Artificial rain can be caused by spraying oppositely charged colloidal dust or sand particles over a cloud. The colloidal water particles present in the cloud will be neutralized and coagulate to form bigger water drops causing artificial rain.

(e) **Formation of delta:** We know that a delta is formed where the flowing river water meets the sea. River water contains suspended particles of sand and clay and sea water contains many electrolytes such as NaCl, KCl, etc. When river water meets sea water, the suspended colloidal impurities are coagulated by the electrolytes present in the sea water to form the delta.

(f) **Fertile soil:** Soil contains many minute particles, both organic and inorganic in nature and is hence colloidal in nature. Fertile soils contain clay minerals, oxides of iron and aluminium and other amorphous minerals. Colloidal soil may develop positive or negative electrostatic charge depending on the nature of the suspended nutrients. Organic colloidal material made up from decomposed and organic material is called humus, and is responsible for retaining water and nutrients in the soil. Humus thus acts as a protective colloid.

2. **Colloids as food articles:** Various food articles are colloids of different types. These include milk, fruit juices, butter, ice cream, etc.
3. **Biocolloids:** Colloidal mixtures of plant and animal origin are biocolloids. Blood is a biological fluid that is colloidal in nature. Animal and plant cell can also be considered colloidal in nature where the various components float in cell fluid. Proteins, lipids and other polymeric molecules of biological systems are colloidal in nature. Bleeding due to a cut is stopped by treating with alum or ferric chloride. These ions cause coagulation of blood, thus leading to clot formation and the cut ceases to bleed.

Industrial Applications of Colloids

Some important applications of colloids are:

1. **Electrical precipitation of smoke:** Smoke that comes out of the chimneys of factories or households is a colloidal sol of particles of carbon, dust, and compounds of lead, arsenic, etc., dispersed in air. To precipitate these particles, the smoke is passed through a column/chamber before it is discharged through the chimney. The chamber contains plates or a metal ball which are carrying a charge opposite to the nature of charge on particles present in smoke. These particles get neutralized when they come in contact with the metal ball/plates and are precipitated out. Hot air free from these particles is then released through the chimney. This device used for electrostatic precipitation of smoke is known as *Cottrell smoke precipitator* after its inventor (Fig. 13.23).

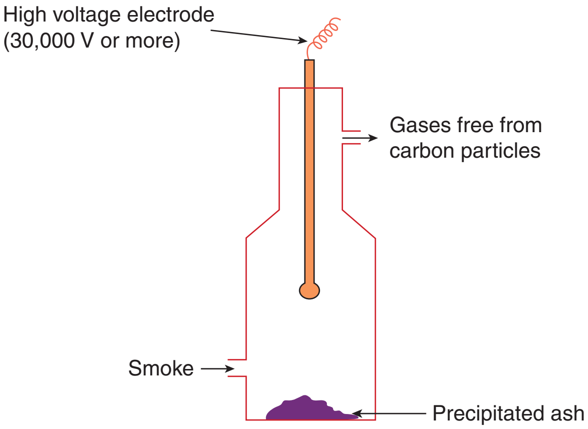


Figure 13.23 Cottrell smoke precipitator.

2. **Purification of drinking water:** The water obtained from natural resources, such as fresh water springs and rivers, has a lot of suspended impurities in them and hence is colloidal in nature. The impurities present are negatively charged clay particles. Alum $[KAl(SO_4)_2 \cdot 12H_2O]$ is used for coagulation of the impurities. Al^{3+} ions from alum neutralize the negative charge of the particles and precipitate them out to settle at the bottom. The clear water is decanted off.
3. **Removal of dirt from sewage:** Sewage contains colloidal particles of dirt, mud, etc. and these colloidal particles a negative charge to it. For treatment of sewage, it is passed through anode plates kept at high potential. The colloidal particles get coagulated due to electrophoresis and can be removed.
4. **Medicines:** Many medicines are colloidal solutions because the drug particles being larger in size are more effective and easily assimilated in the body. Silver sol is known to be an effective germicide and thus is used to destroy viruses, bacteria, fungi and other pathogens. Gold sol is administered as intramuscular injections to improve vitality. It is also used as drug carrier and for detection of tumors. Colloidal antimony is used in treatment of kalazar. Milk of magnesia is an alkaline suspension of magnesium hydroxide used as antacid and laxative. Colloidal sulphur is used for destroying pathogens in plants.
5. **Tanning:** Animal skins/hides are positively charged colloidal systems consisting of extremely fine matrix of collagen fibers dispersed in a fluid phase. In the process of tanning, the collagen fibers are precipitated using a tanning agent (natural tannins or colloidal solution of chromium salts) which is a negatively charged colloidal solution. Mutual coagulation occurs on mixing of two oppositely charged sols and irreversibly changes the chemical nature of the collagen fibers into solid protein fibers. The process of tanning results in hardening of animal hide as leather.
6. **Cleansing action of soaps and detergents:** When soap comes in contact with grease on a soiled surface, the hydrocarbon end of the soap dissolves in the grease, leaving the negatively charged carboxylate end exposed on the grease surface. Since the negatively charged carboxylate groups are strongly attracted by water, small droplets are formed, and the grease is literally lifted or floated away from the soiled object.

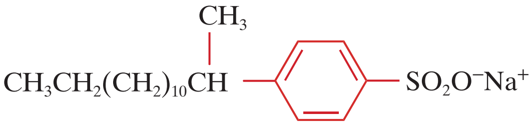
   Detergents are **surfactants** that clean fabric or skin when in dilute solutions. They improve the cleansing properties of water by helping in removal of dirt and oil stuck on fabrics or skin. A detergent consists of two parts: a long hydrocarbon part which is hydrophobic and a short ionic part (containing $-COO^-Na^+$) group which is hydrophilic. When the detergent is added to dirty clothes, the greasy and oily parts stick to the hydrophobic part while the ionic part remain attached to the water. When the dirty clothes are agitated in detergent solution, the hydrophobic part gets washed away and the clothes get cleaned. A soap or detergent is able to dissolve grease by forming micelles from an otherwise insoluble phase.

$CH_3(CH_2)_{10}CH_2SO_2O^-Na^+$

Sodium alkanesulphonates

$CH_3(CH_2)_{10}CH_2OSO_2O^-Na^+$

Sodium alkyl sulphates



Sodium alkylbenzenesulphonates

7. **Photographic plates and films:** Photographic plates are prepared by coating glass plates with emulsion of silver bromide in gelatin that is sensitive to light. In color films, several emulsion layers are separated by filter layers enabling the processing of brilliant colors. The gelatin keeps the silver halide crystals suspended when the emulsion is spread on the plastic film or photographic paper.
8. **Rubber industry:** The latex obtained from rubber trees is an emulsion of negatively charged particles in water. Natural rubber is obtained by coagulation of these particles. For deposition of a rubber layer on any article, the process of electrophoresis is used. The object to be layered with rubber is made into an anode and dipped into latex. The negatively charged particles of rubber get neutralized and deposit on the surface of the article forming a layer.
9. **Industrial products:** Many industrial products such as paints, lubricants, resins, polymers, etc., are also colloidal solutions.

SOLVED OBJECTIVE QUESTIONS FROM PREVIOUS YEAR PAPERS

1. Which of the following statements is correct for lyophilic sols? **(IIT-JEE 2005)**
   (A) The coagulation of the sols is irreversible in nature.
   (B) They are formed by inorganic substances.
   (C) They are self-stabilized.
   (D) They are readily coagulated by addition of electrolytes.

Solution

(C) They are fairly stable and cannot be coagulated easily. Some examples are starch, gum, gelatin, etc. dissolved in a suitable solvent.

2. **Statement 1:** Micelles are formed by surfactant molecules above the critical micellar concentration (CMC).

(IIT-JEE 2007)

Statement 2: The conductivity of a solution having surfactant molecules decreases sharply at the CMC.

(A) Statement 1 is True, Statement 2 is True; Statement 2 is a correct explanation for Statement 1.
(B) Statement 1 is True, Statement 2 is True; Statement 2 is NOT a correct explanation for Statement 1.
(C) Statement 1 is True, Statement 2 is False.
(D) Statement 1 is False, Statement 2 is True.

Solution

(B) Micelles are the cluster or aggregated particles formed by association of colloids in the solution. The formation of micelles takes place only above a particular temperature called Kraft temperature (T_k) and above a particular concentration called critical micelle concentration (CMC). The micelles may contain about 100 molecules or more. The conductivity of the solution decreases sharply at the CMC.

3. Among the following, the surfactant that will form micelles in aqueous solution at the lowest molar concentration at ambient conditions is **(IIT-JEE 2008)**

(A) $CH_3(CH_2)_{15}N^+(CH_3)_3Br$

(B) $CH_3(CH_2)_{11}OSO_3^-Na^+$

(C) $CH_3(CH_2)_6COO^-Na^+$

(D) $CH_3(CH_2)_{11}N^+(CH_3)_3Br^-$

Solution

(A) Critical concentration for micelle formation decreases as the molecular weight of hydrocarbon chain of surfactant grows because in this case, true solubility diminishes and the tendency of surfactant molecules to associate increases.

4. Among the electrolytes Na_2SO_4, $CaCl_2$, $Al_2(SO_4)_3$ and NH_4Cl, the most effective coagulating agent for Sb_2S_3 sol is **(IIT-JEE 2009)**

(A) Na_2SO_4 (B) $CaCl_2$
(C) $Al_2(SO_4)_3$ (D) NH_4Cl

Solution

(C) As Sb_2S_3 is a negative sol, so, $Al_2(SO_4)_3$ will be the most effective coagulant due to higher charge density on Al^{3+} in accordance with Hardy-Schulze rule.
Order of effectiveness of cations: $Al^{3+} > Ca^{2+} > Na^+ > NH_4^+ \cdot NH_4^+$

5. The correct statement(s) pertaining to the adsorption of a gas on a solid surface is (are) **(IIT-JEE 2011)**

(A) Adsorption is always exothermic.
(B) Physisorption may transform into chemisorptions at high temperature.
(C) Physisorption increases with increasing temperature but chemisorptions decreases with increasing temperature.
(D) Chemisorption is more exothermic than physisorption; however, it is very slow due to higher energy of activation.

Solution

(A, B, D)
(A) During adsorption, there is always decrease in surface energy which appears as heat. In other words, we can say that adsorption is an exothermic process.
(B) Physiosorption may transform into chemisorption at high temperature. For example, dihydrogen is first adsorbed on Ni by van der Waals forces, molecules of hydrogen then dissociate to form H atoms, which are held on the surface by chemisorption.
(C) Low temperature is favorable for physiosorption; it decreases with increase of temperature. High temperature is favorable for chemisorption; it increases with increase of temperature.
(D) Energy of adsorption is high in chemisorption which is about 80–240 kJ mol^{-1} as compared to physiosorption where the energy is about 20–40 kJ mol^{-1}.

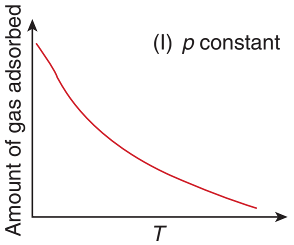
6. Choose the correct reason(s) for the stability of the lyophobic colloidal particles.

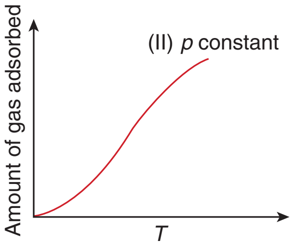
(A) Preferential adsorption of ions on their surface from the solution.
(B) Preferential adsorption of solvent on their surface from the solution.
(C) Attraction between different particles having opposite charges on their surface.
(D) Potential difference between the fixed layer and the diffused layer of opposite charges around the colloidal particles **(IIT-JEE 2012)**

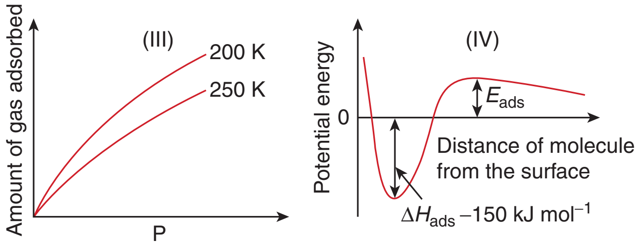
Solution

(A, D) In case of lyophobic sols, the ionic colloid adsorbs ions common to its own lattice during the preparation of the sol. So they are stable and also the potential difference which arises between the fixed layer and the diffused layer makes lyophobic sols more stable.

7. The given graphs/data I, II, III and IV represent general trends observed for different physisorption and chemisorption processes under mild conditions of temperature and pressure. Which of the following choice(s) about I, II, III and IV is (are) correct?







(A) I is physisorption and II is chemisorption.
(B) I is physisorption and III is chemisorption.
(C) IV is chemisorption and II is chemisorption.
(D) IV is chemisorption and III is chemisorption.

(IIT-JEE 2012)

Solution

(A, C) In case of physiosorption, with the increase of temperature and pressure the rate of adsorption decreases because according to Le Chatelier's principle, increase of temperature and pressure will shift the equilibrium to the left

$$\text{Adsorbate} + \text{Adsorbent} \rightleftharpoons \text{Adsorption} + \text{Heat}$$

This is shown in Graphs I and III; whereas in case of chemisorption, there is a formation of strong bond between the adsorbate and the adsorbent and so the rate of adsorption increases with increase in temperature (Graphs II and IV).

8. Methylene blue, from its aqueous solution, is adsorbed on activated charcoal at 25°C. For this process, the correct statement is
(A) The adsorption requires activation at 25°C.
(B) The adsorption is accompanied by a decrease in enthalpy.
(C) The adsorption increases with increase of temperature.
(D) The adsorption is irreversible. **(JEE Advanced 2013)**

Solution

(B) The adsorption of methylene blue on activated charcoal is physisorption, which causes decrease in enthalpy.

9. When O_2 is adsorbed on a metallic surface, electron transfer occurs from the metal to O_2. The **TRUE** statement(s) regarding this adsorption is(are)
(A) O_2 is physisorbed
(B) heat is released
(C) occupancy of π^*_{2p} of O_2 is increased
(D) bond length of O_2 is increased **(JEE Advanced 2015)**

Solution

(B, C, D) During transfer of electrons, adsorption is exothermic. During electron transfer from metal to π^*_{2p} of O_2 molecule, bond order of O_2 decreases; hence O – O bond length increases.

10. Which one of the following characteristics is not correct for physical adsorption? **(AIEEE 2003)**
(A) Adsorption on solids is reversible.
(B) Adsorption increases with increase in temperature.
(C) Adsorption is spontaneous.
(D) Both enthalpy and entropy of adsorption are negative.

Solution

(B) Because adsorption decreases with increase of temperature.

11. The volume of a colloidal particle, V_c as compared to the volume of a solute particle in a true solution V_s could be **(AIEEE 2005)**

(A) $V_c/V_s \approx 1$	(B) $V_c/V_s \approx 10^{23}$
(C) $V_c/V_s \approx 10^{-3}$	(D) $V_c/V_s \approx 10^{3}$

Solution

(D) Diameters of the particles in true solution are in the range 10^{-8} to 10^{-7} m, whereas those of colloidal particles lie in the range of 10^{-9} to 10^{-6} m. Hence, by taking particle size as 10^{-6} and 10^{-7}, respectively, V_c/V_s is given by

$$\frac{V_c}{V_s} = \frac{(4/3)\pi(10^{-6}/2)^3}{(4/3)\pi(10^{-7}/2)^3} = \frac{10^{-18}}{10^{-21}} = 10^3$$

12. The disperse phase in colloidal iron (III) hydroxide and colloidal gold is positively and negatively charged, respectively. Which of the following statements is NOT correct? **(AIEEE 2005)**
(A) Magnesium chloride solution coagulates, the gold sol more readily than the iron (III) hydroxide sol.
(B) Sodium sulphate solution causes coagulation in both sols
(C) Mixing the sols has no effect
(D) Coagulation in both sols can be brought about by electrophoresis

Solution

(C) On mixing oppositely charged sols, their charge gets neutralized. Both the sols can be either partially or completely precipitated.

13. In Langmuir's model of a gas on a solid surface **(AIEEE 2006)**
(A) the rate of dissociation of adsorbed molecules from the surface does not depend on the surface covered.
(B) the adsorption at a single site on the surface may involve multiple molecules at the same time.
(C) the mass of gas striking a given area of surface is proportional to the pressure of the gas.
(D) the mass of gas striking a given area of surface is independent of the pressure of the gas.

Solution

(C) Langmuir model shows the dependence of surface coverage of an adsorbed gas on the pressure of gas above the surface at a fixed temperature.

$$\theta = \frac{kp}{1+kp}$$

where p is the pressure of the gas and θ is the fraction of adsorbed sites.

14. Gold numbers of protective colloids A, B, C and D are 0.50, 0.01, 0.10 and 0.005, respectively. The correct order of their protective powers is **(AIEEE 2008)**

(A) D < A < C < B (B) C < B < D < A
(C) A < C < B < D (D) B < D < A < C

Solution

(C) The protective power of lypophilic solution is expressed in terms of gold number. Lesser the gold number greater its protective power.

15. Which of the following statements is incorrect regarding physisorption? **(AIEEE 2009)**

(A) It occurs because of van der Waals forces.
(B) More easily liquefiable gases are adsorbed readily.
(C) Under high pressure, it results in multimolecular layer on adsorbent surface.
(D) Enthalpy of adsorption ($\Delta H_{\text{adsorption}}$) is low and positive.

Solution

(D)

(A) When a gas is held on the surface of solid by van der Waals forces without resulting in the formation of any chemical bond between the adsorbate and adsorbant, it is called physisorption.

(B) Easily liquefiable gases, that is, gases having high critical temperature are adsorbed more strongly because they have stronger van der Waals forces of attraction.

(C) As the layers of the gas can be adsorbed one over the other by van der Waals forces, multimolecular layers are formed under high pressure.

(D) As physisorption involves only van der Waals forces of attraction and no chemical change, the process is exothermic but the enthalpy of adsorption is quite low (20–40 kJ mol^{-1}).

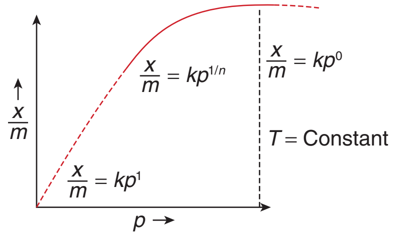
16. According to Freundlich adsorption isotherm, which of the following is correct? **(AIEEE 2012)**

(A) $\dfrac{x}{m} \propto p^0$ (B) $\dfrac{x}{m} \propto p^1$ (C) $\dfrac{x}{m} \propto p^{1/n}$

(D) All the above are correct for different ranges of pressure

Solution

(D) Consider the Freundlich adsorption isotherm shown in the following figure:



From the figure, we have
$x/m \propto p^1$ at low pressure, means straight line at low pressure.
$x/m \propto p^0$ at high pressure means x/m becomes independent of pressure and at moderate pressure $x/m \propto p^n$.

17. 3 g of activated charcoal was added to 50 mL of acetic acid solution (0.06 N) in a flask. After an hour it was filtered and the strength of the filtrate was found to be 0.042 N. The amount of acetic acid adsorbed (per gram of charcoal) is: **(JEE Main 2015)**

(A) 36 mg (B) 42 mg
(C) 54 mg (D) 18 mg

Solution

(D) Initial moles of $CH_3COOH = 0.06 \times 50$
Final moles of CH3COOH = 0.042 × 50
So, the mass of CH_3COOH adsorbed per gram of charcoal =

$$\frac{(0.06-0.042)\times 50\times 10^{-3}\times 60\times 10^{3}}{3} = 18\,\text{mg}$$

REVIEW QUESTIONS

1. What is adsorption? How does it differ from absorption and sorption?

2. Compare the rate and heat of adsorption in physisorption and chemisorption.

3. Explain the effect of increase of temperature on adsorption with the help of a diagram.

4. Show that the effects produced on the extent of adsorption by changing temperature and pressure are consistent with Le Chatelier's principle.

5. What is the driving force for adsorption?

6. What is Freundlich adsorption isotherm? Give its mathematical expression.

7. What is the role of adsorbents in catalysis?

8. Why a catalyst in the finely divided form is preferred?

9. What is the relationship between the adsorption of solutes from solution and the concentration of the solution?

10. Why adsorption of gases is not monolayered at high pressure and low temperature?

11. Draw the five different types of adsorption which take place at high pressure.

12. What is Langmuir's theory of adsorption of gases on solid surface?

13. What is the effect of temperature and nature of solute and adsorbent on the adsorption of dissolved solutes from solution by solids?

14. Prove that Freundlich's adsorption isotherm is a unimolecular adsorption of gas molecules on the adsorbing solid.

15. Classify adsorption on the basis of forces of interaction between adsorbent and adsorbate. Explain their main characteristics.

16. How does the rate of enzyme-catalyzed reactions vary with **(a)** temperature **(b)** pH? Explain with diagrams.

17. Discuss the role of adsorption in:
- **(a)** ion exchange process for demineralization of water
- **(b)** chromatographic separation
- **(c)** catalysis

18. Explain Hardy-Schulze rule and mention briefly what is meant by coagulation value of an electrolyte.

19. Discuss two methods for each of the following:
- **(a)** Preparation of colloidal solutions.
- **(b)** Purification of colloidal solution.

20. What is shape-selective catalysis? Discuss the role of zeolites as catalysts.

21. What are the factors that influence the adsorption of gases on a solid surface?

22. Discuss the mechanism of adsorption as explained by adsorption theory of heterogeneous catalysis.

23. Discuss the role of colloids in the following natural phenomena: **(a)** Orange–red color of sunset; **(b)** formation of comet tail; **(c)** formation of delta.

24. Define the terms **(a)** electrophoresis, **(b)** dialysis, **(c)** mutual coagulation and **(d)** electro-osmosis.

25. Explain the principle and process of coagulation of lyophilic sols.

26. Explain the BET theory for multilayer adsorption.

27. Explain the following with examples: **(a)** Kraft temperature; **(b)** coagulation value.

28. Give reasons for the following:
- **(a)** Ordinary filter papers cannot be used for purification of colloids.
- **(b)** Bleeding from a fresh cut can be stopped by applying alum.
- **(c)** Cottrell's smoke precipitator is used at the mouth of chimneys in factories.
- **(d)** Physical adsorption is multilayered while chemisorption is unilayered.

NUMERICAL PROBLEMS

1. In an experiment, 200 mL of 0.5 M oxalic acid is shaken with 10 g of activated charcoal and filtered. The concentration of the filtrate is reduced to 0.4 M. What is the amount of adsorption?

2. A 0.016 M of an acid solution in benzene is dropped on a water surface, the benzene evaporates and the acid forms a monomolecular film of solid type. What volume of the above solution would be required to cover a 500 cm^2 surface area of water with monomolecular layer of acid ? Area covered by single acid molecule is 0.2 cm^2.

3. The following data is for adsorption of a gas on a solid at 25°C. Confirm that it obeys Langmuir adsorption isotherm. Find the values of k_1 and k_2.

4. Predict whether the following data for the adsorption of a gas on solid at 0°C follows Freundlich adsorption isotherm. If yes, what are the values of k and n?

5. As monomolecular adsorption, how much ammonia in mL at STP would be adsorbed on the surface of 25 g charcoal? Diameter of ammonia molecule is 0.3 nm.

6. Check the applicability of Freundlich adsorption isotherm for the adsorption of solute on a solid at 25°C and find the values of k and n.

Concentration (mol L^{-1})	0.05	0.10	0.50	1.00	1.50
x/m (g)	0.048	0.072	0.144	0.192	0.228

7. A solution of palmitic acid (M = 256 g mol^{-1}) in benzene contains 4.24 g of acid per dm^3. When this solution is dropped on a water surface the benzene evaporates and the palmitic acid forms a mono molecular film of the solid type. If we wish 10 cover an area of 500 cm^2 with a monolayer, what volume of solution should be used? The area covered by one palmitic acid molecule may be taken to be 0.21 nm^2.

8. When 50 mL of 1 M oxalic acid (molecular mass = 126 g mol^{-1}) is shaken with 0.5 g of wood charcoal. The final concentration of the solution after adsorption is 0.5 M. Calculate the amount of the oxalic acid adsorbed per gram of charcoal.

9. In adsorption of hydrogen over a sample of copper monolayer formation volume per gram of powder was found to be 1.36 cm^3 measured al STP. Calculate the specific surface area of copper. Liquid hydrogen has a density of 0.07 g cm^{-3}.

10. When 6×10^{-5}g of a protective colloid was added to 20 mL of a standard gold sol, the precipitation of latter was just prevented on addition of 2 mL of 10% NaCl solution. Calculate the gold number of the protective colloid.

11. A particle of radius 1 cm is broken to form colloidal particles of radius 1000 Å. Calculate the number of colloidal particles produced and their total surface area.

ADDITIONAL OBJECTIVE QUESTIONS

Single Correct Choice Type

1. The process which is catalyzed by one of the products is called
(A) acid–base catalysis. (B) autocatalysis.
(C) negative catalysis. (D) homogeneous catalysis.

2. The colloidal system consisting of a liquid as dispersed phase in a solid as dispersion medium is termed as
(A) aerosol. (B) gel.
(C) emulsion. (D) foam.

3. Silver iodide is used for producing artificial rain because AgI
(A) is easy to spray at high attitudes.
(B) is easy to synthesize.
(C) has crystal structure similar to ice.
(D) is insoluble in water.

4. Bleeding is stopped by the application of ferric chloride. This is because
(A) the blood starts flowing in opposite direction.
(B) the blood reacts and forms a solid, which seals the blood vessel.
(C) the blood is coagulated and thus the blood vessel is scaled.
(D) the ferric chloride seals the blood vessel.

5. 10% sites of the catalyst bed was adsorbed. On heating, gas H_2 is evolved from sites and collected at 0.03 atm and 300 K in a small vessel of 2.46 mL. The number of sites available is 6×10^5 per surface area, and the surface area is 1000 cm^3. Find out the number of surfaces sites occupied per molecule of H_2.
(A) 1 (B) 2
(C) 3 (D) 4

6. Which of the following electrolytes will have maximum flocculation value for $Fe(OH)_3$ sol?
(A) NaCl (B) Na_2S
(C) $(NH_4)_3PO_4$ (D) K_2SO_4

7. The surfactant that will form micelles in aqueous solution at the lowest molar concentration at ambident conditions is
(A) $CH_3(CH_2)_{15}\overset{+}{N}(CH_3)_3Br^-$
(B) $CH_3(CH_2)_{11}OSO_3^-Na^+$
(C) $CH_3(CH_2)_6COO^-Na^+$
(D) $CH_3(CH_2)_{11}\overset{+}{N}(CH_3)_3Br^-$

8. On adding few drops of dilute HCl to freshly precipitated ferric hydroxide, a red colored colloidal solution is obtained. This phenomenon is known as
(A) peptization. (B) dialysis.
(C) protective action. (D) dissolution.

9. 100 mL of 0.6 M acetic acid is shaken with 2 g activated carbon. The final concentration of the solution after adsorption is 0.5 M. What is the amount of acetic acid adsorbed per gram of carbon?
(A) 0.6 g (B) 0.3 g
(C) 1.2 g (D) 1.8 g

10. The color of the colloidal particles of gold by different methods differ because of
(A) variable valency of gold.
(B) different concentration of gold particles.
(C) different type of impurities.
(D) different diameters of colloidal particles.

11. Lyophilic solutions are more stable than lyophobic solutions because
(A) the colloidal particles have positive charge.
(B) the colloidal particles have negative charge.
(C) the colloidal panicles are solvated.
(D) there are strong electrostatic repulsions between the negatively charged colloidal particles.

12. A colloidal system has particles of what size?
(A) 10^{-4} m to 10^{-9} m (B) 10^{-5} m to 10^{-7} m
(C) 10^{-6} m to 10^{-9} m (D) 10^{-6} m to 10^{-7} m

13. When a colloidal solution is observed under an ultramicroscope, we can see
(A) light scattered by colloidal particles.
(B) size of the particle.
(C) shape of the particle.
(D) relative size of the particles.

14. The stabilization of the dispersed phase in a lyophobic sol is due to
(A) the viscosity of the medium.
(B) the surface tension of the medium.
(C) liking for the medium.
(D) the formation of an electrical layer between the two phases.

15. Heat evolved during chemisorption lies in the range of
(A) 4–20 kJ mol^{-1} (B) 40–400 kJ mol^{-1}
(C) 20–40 kJ mol^{-1} (D) 500–1000 kJ mol^{-1}

16. In an adsorption experiment, a graph between log (x/m) vs. log p was found to be linear with a slope of 1.0. The intercept on the log axis was found to be 0.3010. What will be the amount of gas adsorbed per gram of charcoal under a pressure of 0.5 atm.
(A) 1 (B) 2
(C) 3 (D) 4

17. 1 mol of $[AgI]I^-$ can be coagulated by
(A) 1 mol of $Pb(NO_3)_2$ (B) 1/2 mol of $Pb(NO_3)_2$
(C) 2/3 mol of $Pb(NO_3)_2$ (D) None of these

18. Identify the correct statement regarding enzymes.
(A) Enzymes are specific biological catalysts that can normally function at very high temperature.

(B) Enzymes are normally heterogeneous catalysts that are very specific in action.
(C) Enzymes are specific biological catalysts that cannot be poisoned.
(D) Enzymes are biological catalysts that possess well-defined active site.

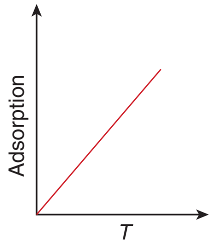
19. Graph between $\log(x/m)$ and $\log p$ is a straight line inclined at an angle $\theta = -45°$. When the pressure of 0.5 atm and $\log k = 0.699$, the amount of solute absorbed per g of adsorbent will be
(A) 1 g/g absorbent
(B) 1.5 g/g adsorbent
(C) 2.5 g/g adsorbent
(D) 0.25 g/g adsorbent

20. There is desorption of physical adsorption when
(A) temperature is increased.
(B) temperature is decreased.
(C) pressure is increased.
(D) concentration is increased.

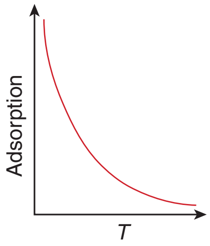
21. The rate of chemisorption
(A) decreases with increase of pressure.
(B) increases with increase of pressure.
(C) is independent of pressure.
(D) is independent of temperature.

22. Which of the following represents the variation of physical adsorption with temperature?

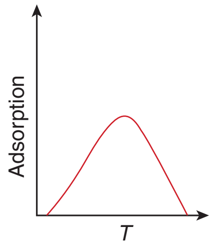
(A)



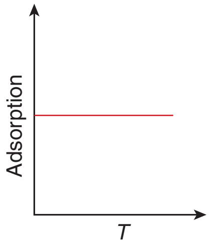
(B)



(C)



(D)



23. Which of the following kinds of catalysis can be explained by the adsorption theory?
(A) Heterogeneous catalysis
(B) Enzyme catalysis
(D) Homogeneous catalysis
(D) Acid–base catalysis

24. 3.6 g of oxygen is adsorbed on 1.2 g of metal powder. What volume of oxygen adsorbed per gram of the adsorbent at STP?
(A) 0.19 L
(B) 1 L
(C) 2.1 L
(D) 3.1 L

25. A while precipitate of $Sn(OH)_4$ is peptized with dil. HCl. The sol particle will carry
(A) positive charge.
(B) negative charge.
(C) sometimes positive and sometimes negative charge
(D) no charge

26. When $FeCl_3$ solution is added to NaOH, a negatively charged sol is obtained. It is due to the
(A) presence of basic group.
(B) preferential adsorption of OH^- ions.
(C) self-dissociation.
(D) electron capture by sol particles.

27. At 400 K energy of activation of a reaction is decreased by 0.8 kcal in the presence of catalyst. Hence, the rate will be
(A) increased by 2.71 times.
(B) increased by 1.18 times.
(C) decreased by 2.72 times.
(D) increased by 6.26 times.

28. Adsorption of gases on solid surface is generally exothermic because
(A) free energy increases.
(B) entropy decreases.
(C) entropy increases.
(D) interaction developed between gas and solid particles.

29. Which gas will be adsorbed on a solid to greater extent?
(A) Gas having non-polar molecule.
(B) Gas having highest critical temperature.
(C) Gas having lowest critical temperature.
(D) Gas having lowest critical pressure.

30. For the coagulation of 100 mL of arsenous sulphide sol, 4 mL of 1 M NaCl is required. What would be the flocculation value of NaCl?
(A) 40
(B) 20
(C) 60
(D) 80

31. The extra stability of lyophilic colloids is due to
(A) charge on their particles.
(B) a layer of medium of dispersion on their particles.
(C) the smaller size of their particles.
(D) the large size of their particles.

32. A catalyst added to a reversible reaction
(A) changes the position of equilibrium.
(B) increases the concentration of products.
(C) increases the equilibrium constant.
(D) speeds up both forward and backward reactions.

33. Gold sol is negatively charged. The flocculation values of effective ions vary in the order:
(A) $Sn^{4+} < Al^{3+} < Ba^{2+} < Na^+$
(B) $PO_3^{3-} < SO_4^{2-} < Cl^-$
(C) $Na^+ > Al^{3+} > Ba^{2+} > Sn^{4+}$
(D) $SO_4^{2-} < Na^+ < PO_4^{3-} < Ba^{2+}$

34. One gram of activate carbon has a surface area of 1000 m^2. Considering complete coverage as well as monomolecular adsorption, how much ammonia at STP would be absorbed on the surface of 44/7 g carbon if a radius of ammonia molecule is 10^{-8} cm.
(A) 7.46 L
(B) 0.33 L
(C) 44.8 L
(D) 23.5 L

35. On addition of 1 mL solution of 10% NaCl to 10 mL gold sol in the presence of 0.250 g of starch, the coagulation is just prevented. Starch has the following gold number:
(A) 0.025
(B) 0.25
(C) 2.5
(D) 250

36. The coagulation power of an electrolyte for As_2S_3 decreases in the order
(A) Ni^+, Al^{3+}, Ba^{2+}
(B) Cl^-, SO_4^{2-}, PO_4^{3-}
(C) Al^{3+}, Ba^{2+}, Na^+
(D) PO_4^{3-}, Cl^-

37. Which type of a property is the Brownian movement of colloidal solution?
(A) Electrical
(B) Optical
(C) Mechanical
(D) Colligative

38. The volume of gases adsorbed by 1 g of charcoal at 300 K are in the order
(A) $H_2 > CO_2 > NH_3$
(B) $NH_3 > H_2 > CO_2$
(C) $NH_3 > CO_2 > H_2$
(D) $CO_2 > NH_3 > H_2$

39. Flocculation value is expressed in terms of
(A) millimol L^{-1}
(B) mol L^{-1}
(C) g L^{-1}
(D) mol mL^{-1}

40. A catalyst in the finely divided form is most effective because
(A) less surface area is available.
(B) more active sites are formed.
(C) more energy gets stored in the catalyst.
(D) none of these.

41. Gels on standing exude small amounts of liquid. This phenomena is known as
(A) efflorescence.
(B) synercsis.
(C) thixotropy.
(D) adsorption.

42. Which of the following electrolytes is least effective in causing flocculation of ferric hydroxide solution?
(A) $K_3[Fe(CN)_6]$
(B) K_2CrO_4
(C) KBr
(D) K_2SO_4

43. Separation of colloidal particles from those of molecular dimension is known as
(A) electrolysis.
(B) electrophoresis.
(C) electrodialysis.
(D) electrosmosis.

44. The protective power of lyophilic sol is
(A) dependent on the size of colloidal particles.
(B) expressed in terms of gold number.
(C) expressed by x/m.
(D) directly proportional to the magnitude of charge on it.

45. The surface area of a catalyst of which adsorb 100 mL of N_2 at STP per gram in order to from a monomolecular layer. The effective surface area occupied by nitrogen molecule on the surface of catalyst is 0.16.
(A) 43.04×10^5 cm^2
(B) 0.18×10^{-15} cm^2
(C) 42×10^5 cm^2
(D) 0.19×9^{-15} cm^2

46. Rate of physisorption increases with
(A) decrease in temperature.
(B) increase in temperature.
(C) decrease in pressure.
(D) decrease in surface area.

47. Lyophilic sols are
(A) irreversible sols.
(B) prepared from inorganic compounds.
(C) coagulated by adding electrolytes.
(D) self-stabilizing.

Multiple Correct Choice Type

1. Select the correct statement(s):
(A) Physical adsorption is multilayer, non-directional.
(B) Chemical adsorption highly specific in nature.
(C) Physical adsorption is due to free valence of atoms.
(D) Chemical adsorption is due to stronger interaction or bond formation.

2. Which of the following is the application of adsorption?
(A) Deionization of water
(B) Gas masks
(C) Hygroscopic nature of $CaCl_2$
(D) Heterogeneous catalysis

3. Which of the following statements are correct?
(A) Flocculation value is inversely proportional to the coagulating power.
(B) Alum is used for cleaning muddy water.
(C) Milk is an emulsion of protein in water.
(D) Gelatin added to ice cream acts as an emulsifier.

4. Which of the following are accompanied by adsorption?
(A) Decrease in entropy of the system
(B) Decrease in enthalpy of the system
(C) $T\Delta S$ for the process is negative
(D) Increase in enthalpy of the system

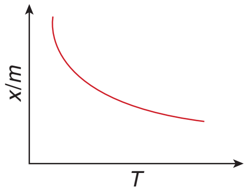
5. Let x be the amount of a gas adsorbed by a fixed amount or a solid. If monolayer adsorption is supposed to occur, then which of the following statements is correct?
(A) At low pressures, x increases more than proportionately to gas pressure.
(B) At low pressure, x increases proportionately to gas pressure.
(C) At moderate pressures, x increases less than proportionately to gas pressure.
(D) At high pressures, x becomes independent of gas pressure.

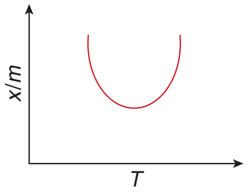
6. Select the correct statement(s)
(A) Adsorption is a non-spontaneous process.

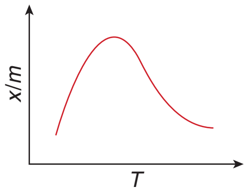
(B) Surface energy decreases during the process of adsorption.
(C) Adsorption takes place with decrease of entropy.
(D) In general, adsorption is exothermic process.

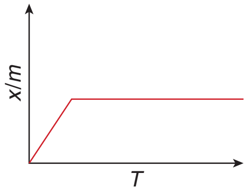
7. Point out the correct statement.
(A) Brownian motion and Tyndall effect are shown by colloidal systems.
(B) The colloidal solution of a liquid in liquid is called emulsion.
(C) Hardy–Schulze law is related with coagulation of a sol.
(D) Higher is the gold number, greater will be the protective power of a lyophilic colloid.

8. Which plot among the following do not represent adsorption isobar for chemisorption?

(A)


(B)


(C)


(D)


9. Which of the following are correct?
(A) (x/m) = constant at high pressure
(B) Constant $(x/m) = p^{1/n}$ (at intermediate pressure)
(C) Constant $(x/m) = p^{n}$ (at low pressure)
(D) Constant $(x/m) = p^{1/n}$ (at high pressure)

10. Colloidal solution can be purified by
(A) dialysis.
(B) electrodialysis.
(C) electrophoresis.
(D) ultrafiltration.

11. Which of the following decrease the activation of a solid adsorbent?
(A) Subdividing the solid adsorbent.
(B) Polishing the surface of the solid adsorbent.
(C) Carrying out the adsorption at very high temperature.
(D) Blowing superheated steam through the porous adsorbent.

12. Coagulation of colloids can be achieved by
(A) centrifugation. (B) adding electrolyte.
(C) change in pH. (D) adding water.

Assertion–Reasoning Type

Choose the correct option from the following:
(A) Statement 1 is True, Statement 2 is True; Statement 2 is the correct explanation for Statement 1.
(B) Statement 1 is True, Statement 2 is True; Statement 2 is NOT the correct explanation for Statement 1.
(C) Statement 1 is True, Statement 2 is False.
(D) Statement 1 is False, Statement 2 is True.

1. **Statement 1:** Physical adsorption of molecules on the surface requires activation energy.
Statement 2: Because the bonds of adsorbed molecules are broken.

2. **Statement 1:** Small quantity of soap is used to prepare a stable emulsion.
Statement 2: Soap lowers the interfacial tension between oil and water.

3. **Statement 1:** A sol of As_2S_3 prepared by the action of H_2S on As_2S_3 is negatively charged.
Statement 2: It is due to the adsorption of H^+ ions on the surface of the colloidal particle and S^{2-} ions in the diffused layer.

4. **Statement 1:** Activity of an enzyme is pH dependent.
Statement 2: Change in pH affects the solubility of the enzyme in water.

5. **Statement 1:** Aqueous gold colloidal solution is red in color.
Statement 2: The color arises due to scattering of light by colloidal gold particles.

6. **Statement 1:** Poisonous gases such as SO_2, Cl_2, CH_4, etc., from the atmosphere displace O_2, N_2 gases already adsorbed by the charcoal in the gas masks.
Statement 2: A strongly adsorbed gas is displaced by a weakly adsorbed gas.

7. **Statement 1:** A lyophilic colloidal sol is more stable than a lyophobic col.
Statement 2: A lyophilic sol is solvated to a much greater extent in comparison to lyophobic sol.

Comprehension Type

Read the paragraphs and answer the questions that follow.

Paragraph I

The aggregation of $Fe(OH)_3$ sol can be done by adding ionic solution, especially if the solution contains multiple-charged anions (e.g., phosphate ions). Coagulation is the process by which the dispersed phase of a colloid undergoes aggregation, and thus separates from the continuous phase.

1. The electrolyte that has the least effect in the coagulation of $Fe(OH)_3$ is
(A) potassium carbonate. (B) sodium sulphate.
(C) potassium ferrocyanide. (D) potassium iodide.

2. Colloidal sulphur particles are negatively charged with thiosulphate ions, $S_2O_3^{2-}$, and other ions on the surface of the sulphur. Indicate which of the following would be most effective in coagulating colloidal sulphur.
(A) NaCl (B) KCl
(C) $MgCl_2$ (D) $Al_2(SO_4)_3$

3. Which of the following solution is negatively charged?
(A) Arsenious sulphide
(B) Aluminium hydroxide
(C) Ferric hydroxide
(D) Silver iodide in silver nitrate solation

4. Which of the following anions will have minimum flocculation value for the ferric oxide solution?
(A) Cl^- (B) Br^-
(C) SO_4^{2-} (D) $[Fe(CN)_6]^{3-}$

Paragraph II

The adsorption is called physical adsorption or physisorption if the accumulation of gas on the surface of a solid occurs due to weak van der Waals forces. The adsorption is called chemical adsorption or chemisorption when the gas molecules or atoms are held to the solid surface by chemical bonds that are either ionic or covalent. Chemisorption is often referred to as activated adsorption because it has a rather high energy of activation.

5. Which of the following is not a characteristic of chemisorption?
(A) Adsorption is irreversible.
(B) ΔH is of the order of 400 kJ.
(C) Adsorption is specific.
(D) Adsorption increases with increase of surface area.

6. Physical adsorption is appreciable at
(A) higher temperature (B) lower temperature.
(C) room temperature. (D) none of these.

7. The rate of chemisorption
(A) decreases with increase of pressure.
(B) is independent of pressure.
(C) is maximum at one atmospheric pressure.
(D) increases with increase of pressure.

Integer Answer Type

The answer is a **non-negative integer**.

1. In an experiment, addition of 4.0 mL of 0.005 M $BaCl_2$ to 16.0 mL of arsenius sulphide sol just causes the complete coagulation in 2 h. The flocculating value of the effective ion is ________.

2. The number of phases present in a colloidal solution is ________.

3. The coagulation of 100 mL of a colloidal solution of gold is completely prevented by adding 0.08 g of starch to it before adding 10 mL of 10% NaCl solution. The gold number of starch is ________.

4. Among the following, the number of substances that will adsorb water vapor is ________.

Silica, alumina, charcoal, calcium chloride, calcium carbonate, powdered cellulose, Kieselguhr, Fuller's earth.

Matrix–Match Type

1. Match the colloidal dispersion with the nature of dispersion.

Column I	Column II
(A) Milk	(p) Solid in liquid
(B) Mist	(q) Liquid in gas
(C) Gold sol	(r) Solid in solid
(D) Ruby glass	(s) Liquid in liquid

2. Match the type of adsorption with its characteristics.

Column I	Column II
(A) Physisorption	(p) Not very specific and decreases with temperature.
(B) Chemisorption	(q) Specific and increases with temperature.
(C) Desorption of a solute on liquid	(r) Increases the surface tension of the liquid surface
(D) Adsorption of a solute on a liquid	(s) Decreases the surface tension of the liquid surface.
	(t) Adsorption is due to stronger interaction or bond formation

3. Match the technique with its application.

Column I	Column II
(A) Bredig's arc method	(p) Movement of ions across the membrane in presence of electric field
(B) Electrodialysis	(q) Preparation of metals sols
(C) Ultracentrifugation	(r) Purification of sols
(D) Peptization	(s) Preparation of sols
	(t) The precipitate adsorbs one of the ions of the electrolyte on its surface

4. Match the sol with its type.

Column I	Column II
(A) Gelatin sol	(p) Lyophilic
(B) Gold sol	(q) Associated
(C) Soap sol	(r) Multimolecular
(D) Starch sol	(s) Macromolecular

ANSWERS

Review Questions

8. Increase in surface area increases rate of adsorption.

9. $x/m = kC^{(1/n)}$

16. On increasing the temperature and pH, the rate increases, becomes maximum at 37°C and pH = 7.4 and after that it falls down.

21. Nature of adsorbate, nature of adsorbent, surface area of the adsorbent and pressure of the gas.

Numerical Problems

1. $0.18 \text{ mol m}^{-2} \text{ g}^{-1}$
2. 25.94×10^{-3} mL
3. $k_1 = 0.23 \text{ torr}^{-1}$ and $k_2 = 0.93 \text{ mL}^{-1}$
4. $k = 8.9$ and $n = 2$
5. 13153.5 mL
6. $k = 0.19$ and $n = 2.29$
7. $2.493 \times 10^{-5} \text{ dm}^3$
8. 6.30 g
9. $5.78 \times 10^4 \text{ cm}^2$
10. 0.03
11. 10^{15}; $12 \times 10^3 \text{ cm}^2$

Additional Objective Questions

Single Correct Choice Type

1. (B)
2. (B)
3. (C)
4. (D)
5. (C)
6. (A)
7. (A)
8. (A)
9. (B)
10. (D)
11. (C)
12. (C)
13. (A)
14. (D)
15. (C)
16. (A)
17. (B)
18. (B)
19. (C)
20. (A)
21. (B)
22. (B)
23. (A)
24. (C)
25. (A)
26. (B)
27. (C)
28. (D)
29. (B)
30. (A)
31. (B)
32. (D)
33. (A)
34. (A)
35. (D)
36. (C)
37. (C)
38. (C)
39. (A)
40. (B)
41. (B)
42. (C)
43. (C)
44. (B)
45. (A)
46. (A)
47. (D)

Multiple Correct Choice Type

1. (B, D)
2. (A, B, D)
3. (A, B, D)
4. (A, B, C)
5. (B, C, D)
6. (B, C, D)
7. (A, B, C)
8. (A, B, D)
9. (A, B)
10. (A, B, D)
11. (B, C)
12. (A, B, C)

Assertion–Reasoning Type

1. (D)
2. (A)
3. (C)
4. (B)
5. (A)
6. (A)
7. (A)

Comprehension Type

1. (C)
2. (D)
3. (B)
4. (D)
5. (B)
6. (B)
7. (D)

Integer Answer Type

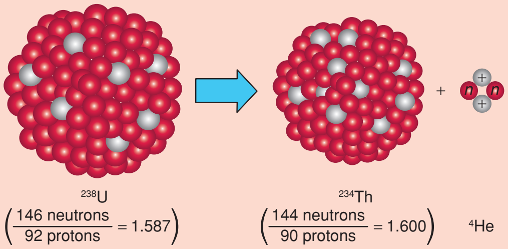
1. (1)
2. (2)
3. (8)
4. (5)

Matrix–Match Type

1. A → (s); B → (q); C → (p), D → (r)
2. A → (p); B → (q, t); C → (r), D → (s)
3. A → (q); B → (r); C → (r), D → (q, t)
4. A → (p, r); B → (r); C → (q), D → (p, s)

14

Nuclear Chemistry


^{238}U
$\left(\frac{146 \text{ neutrons}}{92 \text{ protons}} = 1.587\right)$
^{234}Th
$\left(\frac{144 \text{ neutrons}}{90 \text{ protons}} = 1.600\right)$
+
^{4}He

α-particle decay in neutron-poor nuclide ^{238}U

Contents

14.1 Radioactivity
14.2 Structure of Atom
14.3 Stability of Nucleus
14.4 Modes of Radioactive Decay
14.5 Decay Mechanism in Neutron-Rich and Neutron-Poor Nuclides
14.6 Binding Energy and Nuclear Stability
14.7 The Kinetics of Radioactive Decay
14.8 Radioactive Equilibrium
14.9 Activity of Radioactive Substances, Detection and Units of Radioactivity
14.10 Natural vs. Induced Radioactivity
14.11 Transmutation
14.12 Nuclear Reactions
14.13 Biological Effects of Radiation
14.14 Applications of Radioactivity

The discovery of X-rays by William Conrad Roentgen in November of 1895 excited the imagination of a generation of scientists who rushed to study this phenomenon. Within a few months, Henri Becquerel found that both uranium metal and salts of this element gave off a different form of radiation, which could also pass through solids. This was based on his observation that photographic plates developed bright spots when exposed to uranium metal. By 1898, Marie Curie found that compounds of thorium also gave out radiations. After painstaking effort, she eventually isolated two more radioactive elements—polonium and radium—from ores that contained uranium. She and her husband Pierre Curie, named this phenomenon as **radioactivity**. They also proposed that radioactivity was a nuclear property that was characteristic of unstable or excited nucleus. The property is independent of the conditions of pressure and temperature and depends only on the amount of unstable atom present.

In this chapter, we will study about the nature of radioactive radiations, the cause of radioactivity, theory and rate of radioactive decay, nature of nuclear fission and fusion reactions and applications of radioactivity.

14.1 | RADIOACTIVITY

In 1899, Ernest Rutherford found that there were at least two different forms of radioactivity when he studied the absorption of radioactivity by thin sheets of metal foil. One, which he called *alpha* (α)*-particles*, was absorbed by metal foil that was a few hundredths of a centimeter thick. The other, *beta* (β)*-particles*, could pass through 100 times as much metal foil before they became absorbed. Shortly thereafter, a third form of radiation, *gamma* (γ)*-rays*, was discovered that could penetrate as much as several centimeters of lead.

The results of early experiments on these three forms of radiation are summarized in Fig. 14.1. The direction in which α-particles were deflected by an electric field suggested that they were positively charged. The magnitude of this deflection suggested that they had the same charge-to-mass ratio as an He^{2+} ion. To test the equivalence between α-particles and He^{2+} ions, Rutherford built an apparatus that allowed α-particles to pass through a very thin glass wall into an evacuated flask that contained a pair of metal electrodes. After a few days, he connected these electrodes to a battery and noted that the gas in the flask did indeed give off the characteristic emission spectrum of helium.

Experiments with electric and magnetic fields demonstrated that β-particles were negatively charged. Furthermore, they had the same charge-to-mass ratio as an electron. To date, no detectable difference has been found between β-particles and electrons. The only reason to retain the name β-particle is to emphasize the fact that these particles are ejected from the nucleus of an atom when it undergoes radioactive decay.

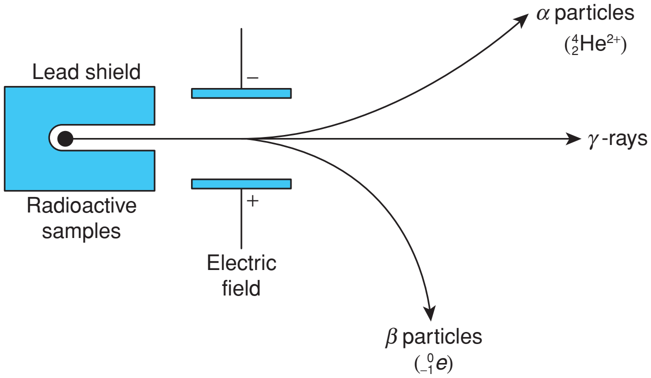


Figure 14.1 The effect of an electric field on α, β, and γ-radiation.

The fact that γ-rays are not deflected by either electric or magnetic fields suggests that these rays do not carry an electric charge. Since they travel at the speed of light, they are classified as a form of electromagnetic radiation that carries even more energy than X-rays.

Theory of Nuclear Disintegration

At the turn of the twentieth century, when radioactivity was discovered, atoms were assumed to be indestructible. Ernest Rutherford and Frederick Soddy, however, found that radioactive substances became less active with time (Fig. 14.2). More importantly, they noticed that radioactivity was always accompanied by the formation of atoms of a different element. By 1903, they concluded that radioactivity was accompanied by a change in the structure of the atom. They therefore assumed that radiation was emitted when an element decayed into a different kind of atom.

By 1910, there were 40 radioactive elements isolated which were associated with the decay process uranium metal to lead. This created a problem, however, because there was space for only 11 elements between lead and uranium. In 1913, Kasimir Fajans and Frederick Soddy proposed an explanation for these results based on the following rules.

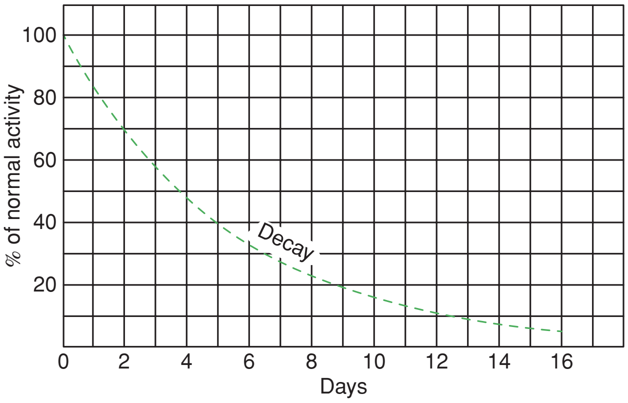


Figure 14.2 Decay curve reported by Rutherford and Soddy for "uranium X," produced when uranium undergoes radioactive decay.

1. Emission of an α-particle produces an element that is four mass units lighter and the atomic number decreases by two. The daughter element is, therefore, two places to the left of the parent in the periodic table.
2. When a β-particle is emitted, the mass number remains the same. However, the atomic number increases by one and the new element is one place to the right of the parent in the periodic table. These changes are shown in the following series:

$$^{223}_{88}\mathrm{Ra} \xrightarrow{\alpha} {}^{219}_{86}\mathrm{Rn} \xrightarrow{\alpha} {}^{215}_{84}\mathrm{Po} \xrightarrow{\alpha} {}^{211}_{82}\mathrm{Pb} \xrightarrow{\beta} {}^{211}_{83}\mathrm{Bi} \xrightarrow{\alpha} {}^{207}_{81}\mathrm{Tl} \xrightarrow{\beta} {}^{207}_{82}\mathrm{Pb}$$

3. Radioactive elements that fall in the same place in the periodic table are different forms of the same element. The radioactive thorium produced by the α-particle decay of uranium is a different form of the element than the radioactive thorium obtained by the β-particle decay of actinium.

Soddy proposed the name *isotope* to describe different radioactive atoms that occupy the same position in the periodic table. J. J. Thomson and Francis Aston then used a mass spectrometer to show that isotopes are atoms of the same element that have different atomic masses. To understand the cause of phenomenon of radioactivity, we need to first consider the structure of the nucleus and the stability of nucleus.

14.2 | STRUCTURE OF ATOM

The discovery of the electron in 1897 by J.J. Thomson suggested that there is an internal structure to the "indivisible" building blocks of matter known as atoms. This raised an obvious question: How many electrons does an atom contain? By studying the scattering of light, X-rays and α particles, Thomson concluded that the number of electrons in an atom is between 0.2 and 2 times the weight of the atom.

In 1911, Rutherford concluded that the scattering of α-particles by extremely thin pieces of metal foil could be explained by assuming that all of the positive charge and most of the mass of the atom are concentrated in an infinitesimally small fraction of the total volume of the atom, for which he proposed the name *nucleus*. Rutherford's data also suggested that the nucleus of a gold atom has a positive charge that is about 80 times the charge on an electron.

The discovery of the neutron in 1932 explained the discrepancy between the charge on the nucleus and the mass of an atom. A neutral gold atom with mass of 197 amu consists of a nucleus that contains 79 protons and 118 neutrons surrounded by 79 electrons. By convention, this information is specified by the following symbol, which describes the only naturally occurring isotope of gold.

Mass number → $^{197}_{79}\text{Au}$ ← Charge on nucleus

This convention can also be applied to elementary particles. Lowercase letters are used to identify the electron, proton, and neutron.

$^{4}_{2}\text{He}$	$^{0}_{-1}e$	$^{1}_{1}p$	$^{1}_{0}n$	(14.1)
α-particle	β-particle or electron	Proton	Neutron	

A particular combination of protons and neutrons is called a **nuclide**.

1. Nuclides with the same number of protons are called isotopes.
2. Nuclides with the same mass number are isobars.
3. Nuclides with the same number of neutrons are isotones.

Apart from isotones, isobars and isotopes, we have two more terms – isodiaphers and isosteres. **Isodiaphers** are those radioactive nuclides that have the same (N – Z) or (A – 2Z) values. For example, $^{39}_{19}\text{K}$ and $^{19}_{9}\text{F}$ ($A - 2Z = 1$); $^{235}_{92}\text{U}$ and $^{231}_{90}\text{Th}$ ($A - 2Z = 51$). **Isosteres** are those molecules that have the same number of atoms as well as electrons. For example, CO_2 and N_2O (atoms = 3, electrons = 22); N_2 and CO (atoms = 2, electrons = 14).

Solved Example 14-1

Classify the following sets of nuclides as examples of isotopes, isobars and isotones: **(a)** ^{12}C, ^{13}C and ^{14}C, **(b)** ^{40}Ar, ^{40}K and ^{40}Ca and **(c)** ^{14}C, ^{15}N and ^{16}O.

Solution

(a) ^{12}C, ^{13}C and ^{14}C are isotopes because they all contain six protons.

(b) ^{40}Ar, ^{40}K and ^{40}Ca are isobars because they have the same mass number.

(c) ^{14}C, ^{15}N and ^{16}O cannot be isotopes because they contain different number of protons. They cannot be isobars, because they have different mass numbers. All of them contain eight neutrons, so they are examples of isotones.

Solved Example 14-2

If $^{a}_{8}\text{X}$ atom is isotone to $^{17}_{9}\text{Y}$ atom, then what is the value of a? Identify elements X and Y also.

Solution

For $^{a}_{8}\text{X}$ to be an isotone to $^{17}_{9}\text{Y}$, their number of neutrons should be the same. So, $a - 8 = 17 - 9 = 8 \Rightarrow a = 16$. Thus, the element X is $^{16}_{8}\text{O}$ and element Y is $^{17}_{9}\text{F}$.

14.3 | STABILITY OF NUCLEUS

The radius of a nucleus is very small, roughly 10^{-15} m. Nuclear distances are measured in femtometres (1 fm = 10^{-15} m). Most atoms are 1–2 Å, that is, 1 to 2×10^{-10} m in radius. The nucleus of oxygen, for example, has a radius of 2.5 fm. Most of the mass of an atom is concentrated in the nucleus. As a result, its density is very high, approximately, 2.4×10^{14} g cm^{-3} or about 10^{13} times the density of the densest element iridium (22.61 g cm^{-3}).

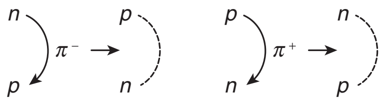
Forces in the Nucleus

Protons have a positive charge. In any nucleus containing two or more protons there will be electrostatic repulsion between the like charges. In a stable nucleus, the attractive forces are greater than the repulsive forces. In an unstable nucleus, the repulsive forces exceed the attractive forces and spontaneous fission occurs. The attractive forces in the nucleus cannot be electrostatic for two reasons:

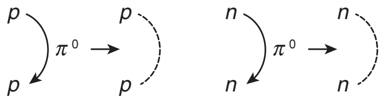
1. There are no oppositely charged particles.
2. The forces only act over a very short distance of 2–3 fm.

If the nuclear particles are separated by a distance much greater than this, attraction ceases. Electrostatic forces diminish only slowly with distance. The attractive force does not depend on the charge as the same attractive force binds protons to protons, protons to neutrons and neutrons to neutrons.

Two nuclear particles are held together by sharing a particle and the particle exchanged is called a π meson. Mesons may have a positive charge π^+, a negative charge π^- or no charge π^0. Exchange of π^- and π^+ mesons accounts for the binding energy between neutrons and protons. The transfer of a charge converts a neutron into a proton or *vice versa*. The resultant attractive forces are indicated by dotted lines in the following examples.



A π^0 meson is exchanged between two protons or between two neutrons.



The attractive forces between *p–n*, *n–n*, and *p–p*, are probably all similar in strength. The different types of mesons have similar masses. The mass of a π^0 meson is 264 times that of an electron. The masses of both π^+ and π^- are equal and about 263 times that of an electron.

Stability

Many nuclei are *unstable* even when they correspond to the ground state. Unstable nuclei decompose by emitting various particles and electromagnetic radiation, and this is called **radioactive decay**. Over 1500 unstable nuclei are known. If no radioactive decomposition can be detected, the nucleus is said to be ***stable***.

The stability of a nucleus depends on the number of protons and neutrons present. Certain combinations of neutrons and protons are particularly stable:

1. **Even number of protons and neutrons:** Elements of even atomic number are more stable and more abundant than neighboring elements of odd atomic number. This is known as **Harkin's rule**. (The rule applies almost universally, but ^{1}H is a notable exception.) Elements of even atomic number are richer in isotopes and never have less than three stable isotopes. Elements with odd atomic numbers often have only one stable isotope and never have more than two. There is a tendency for the number of neutrons and the number of protons in the nucleus to be even (Table 14.1).

   These observations suggest that nucleons in the nucleus are paired in a way similar to pairing of electrons in atomic or molecular orbits for even number of neutrons/protons, the spins are paired so the magnetic fields generated are cancelled. So, the nucleus has lower energy and greater stability.
2. **Filled shell:** Certain nuclei are extra-stable, and this is attributed to a filled shell. Nuclei with 2, 8, 20, 28, 50, 82 or 126 neutrons or protons are particularly stable and have a large number of isotopes. These numbers are termed **magic numbers**. The numbers 114, 164 and 184 should also be included in the series of magic numbers. When both the number of protons and the number of neutrons are magic numbers reorderthe nucleus is very stable. For example, $^{208}_{82}$Pb is very stable since it and has 82 protons, and 208 – 82 = 126 neutrons. $^{20}_{10}$Ne has a magic number of nucleons when both protons and neutrons are counted. $^{4}_{2}$He and $^{16}_{8}$O have magic numbers of both protons and neutrons.

Table 14.1 The number of neutrons, protons and stable nuclei

Number of protons p (= Z)	Number of neutrons n	Number of stable isotopes
Even	Even	164
Even	Odd	55
Odd	Even	50
Odd	Odd	4

3. **Nuclear shell model:** The observation on magic number suggests that nucleus has a shell structure with energy levels similar to electron energy levels. The elements with completely filled energy levels with (2, 8, 18, 32, 50, 72, and 98) electron for $n = 1, 2, \ldots, 7$, respectively, are stable. The magic number of nucleons impact stability to nucleus based on the same logic.

The Ratio of Neutrons to Protons

For elements of low atomic number (up to $Z = 20$, i.e., Ca) the most stable nuclei exist when the nucleus contains an equal number of protons (p) and neutrons (n). This means that the ratio $n/p = 1$. Elements with higher atomic numbers are more stable if they have a slight excess of neutrons as this increases the attractive force and also reduces repulsion between protons. Thus, the ratio n/p increases progressively up to about 1.6 at $Z = 92$ (uranium). In elements with still higher atomic numbers, the nuclei have become so large they undergo spontaneous fission. These trends are shown in the graphs of number of neutrons (n) against number of protons (p), and n/p ratio against number of protons number for the stable nuclei (Fig. 14.3).

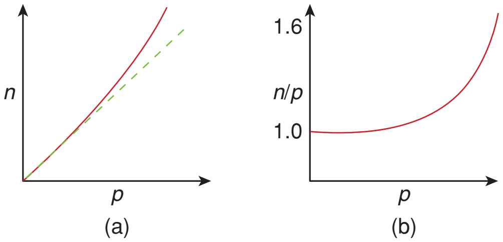


Figure 14.3 Neutron to proton ratio.

Stable nuclei lie near to these curves. Nuclei with n/p ratios appreciably higher or lower than the stable ratio are radioactive. When they decay, they form nuclei closer to the line of maximum stability.

If the n/p ratio is high, the isotope lies above the curve. Such a nucleus will decay in such a way that it reduces the n/p ratio and forms a stable arrangement, thus, emitting a β-particle.

If the n/p ratio is low, the isotope lies below the curve. Such a nucleus will decay in such a way that it increases the n/p ratio and forms a stable arrangement, thus, emitting a positron.

We will first study the various modes of radioactive decay and then explore the decay mechanism adopted by nuclei with different n/p ratio.

Solved Example 14-3

One of the nuclides in each of the following pairs is radioactive; the other is stable. Which one is radioactive and which is stable? Explain.

(a) $^{208}_{84}$Po, $^{209}_{83}$Bi **(b)** $^{39}_{19}$K, $^{40}_{19}$K **(c)** $^{71}_{31}$Ga, $^{76}_{31}$Ga

Solution

(a) $^{209}_{83}$Bi is more stable as n/p ratio is higher;

(b) $^{39}_{19}$K is more stable as number of neutrons is 20 which is magic number;

(c) $^{76}_{31}$Ga is more stable as n/p ratio is higher.

Solved Example 14-4

Which of the nuclides is more stable in **(a)** $^{27}_{13}$Al or $^{29}_{13}$Al, **(b)** $^{23}_{11}$Na or $^{24}_{11}$Na ?

Solution

(a) $^{27}_{13}$Al is more stable because in $^{29}_{13}$Al there are 2 neutron more than that required for stability.

(b) $^{23}_{11}$Na is more stable because in $^{24}_{11}$Na there is 1 neutron more than that required for stability.

Solved Example 14-5

Out of the isobars $^{114}_{48}\text{Cd}$, $^{114}_{49}\text{In}$ and $^{114}_{50}\text{Sn}$, which one is radioactive and why?

Solution

$^{114}_{49}\text{In}$ because it has odd number of neutrons and protons.

14.4 | MODES OF RADIOACTIVE DECAY

Early studies of radioactivity indicated that three different kinds of radiation were emitted, symbolized by the first three letters of the Greek alphabet α, β and γ. With time, it became apparent that this classification scheme was much too simple. The emission of a negatively charged β^- particle, for example, is only one example of a family of radioactive transformations known as β-decay. A fourth category, known as spontaneous fission, also had to be added to describe the process by which certain radioactive nuclides decompose into fragments of different weight.

Alpha Decay

Alpha decay is usually restricted to the heavier elements in the periodic table. (Only a handful of nuclides with atomic numbers less than 83 emit an α-particle.) The product of α-decay is easy to predict if we recognize that both mass and charge are conserved in nuclear reactions. Alpha decay of the ^{238}U "parent" nuclide, for example, produces ^{234}Th as the "daughter" nuclide.

$$^{238}_{92}\text{U} \rightarrow {}^{234}_{90}\text{Th} + {}^{4}_{2}\text{He} \quad (\alpha\text{-decay})$$

The sum of the mass numbers of the products (234 + 4) is equal to the mass number of the parent nuclide (238), and the sum of the charges on the products (90 + 2) is equal to the charge on the parent nuclide.

Beta Decay

Three different modes of β **-decay** can be observed in nature: (a) electron or negatron (β^-) emission, (b) electron capture and (c) positron (β^+) emission.

Electron (β^-) emission is the process in which an electron is ejected or emitted from the nucleus. When this happens, the charge on the nucleus increases by one. Electron (β^-) emitters are found throughout the periodic table, from the lightest elements (^3H) to the heaviest (^{255}Es). The product of β^- emission can be predicted because both mass number and charge are conserved in nuclear reactions. If ^{40}K is a β-emitter, for example, the product of this reaction must be ^{40}Ca.

$$^{40}_{19}\text{K} \rightarrow {}^{40}_{20}\text{Ca} + {}^{0}_{-1}e \quad [\text{negatron}\ (\beta^-)\ \text{emission}]$$

Note: Negatron is negative β-particle, while positron is positive β-particle.

Once again the sum of the mass numbers of the products is equal to the mass number of the parent nuclide and the sum of the charge on the products is equal to the charge on the parent nuclide.

Nuclei can also decay by capturing one of the electrons that surround the nucleus. **Electron capture** leads to a decrease of one in the charge on the nucleus. The energy given off in this reaction is carried by an X-ray photon, which is represented by the symbol $h\nu$, where h is Planck's constant and ν is the frequency of the X-ray. The product of this reaction can be predicted, once again, because mass and charge are conserved.

$$^{40}_{19}\text{K} + {}^{0}_{-1}e \rightarrow {}^{40}_{18}\text{Ar} + h\nu \quad (\text{electron capture})$$

The electron captured by the nucleus in this reaction is usually a 1*s* electron because electrons in this orbital are the closest to the nucleus.

A third form of β-decay is called **positron (β^+) emission**. The positron is the antimatter equivalent of an electron. It has the same mass as an electron but the opposite charge. Positron (β^+) decay produces a daughter nuclide with one fewer positive charge on the nucleus than on the parent.

$$ {}^{40}_{19}\text{K} \rightarrow {}^{40}_{18}\text{Ar} + {}^{0}_{+1}e \quad [\text{positron}\,(\beta^+)\,\text{emission}] $$

Positrons have a very short lifetime. They rapidly lose their kinetic energy as they pass through matter. As soon as they come to rest, they combine with an electron to form two γ-ray photons in a matter–antimatter annihilation reaction.

$$ {}^{0}_{+1}e + {}^{0}_{-1}e \rightarrow 2\gamma $$

Thus, although it is theoretically possible to observe a fourth mode of β-decay corresponding to the capture of a positron, this reaction does not occur in nature.

The three forms of β decay for the ${}^{40}\text{K}$ nuclide are summarized as follows. Note that the mass number of the parent and daughter nuclides are the same for electron emission, electron capture, and positron emission. All three forms of β decay therefore interconvert isobars.

$$ {}^{40}_{19}\text{K} \rightarrow {}^{40}_{20}\text{Ca} + {}^{0}_{-1}e $$
$$ {}^{40}_{19}\text{K} + {}^{0}_{-1}e \rightarrow {}^{40}_{18}\text{Ar} + \gamma + \nu $$
$$ {}^{40}_{19}\text{K} \rightarrow {}^{40}_{18}\text{Ar} + {}^{0}_{+1}e + \nu $$

Gamma Emission

The daughter nuclides produced by α-decay or β-decay are often obtained in an excited state. The excess energy associated with this excited state is released when the nucleus emits a photon in the γ-ray portion of the electromagnetic spectrum. Most of the time, the γ-ray is emitted within 10^{-12} s after the α- or β-particle. In some cases, **γ-emission** is delayed, and a short-lived, or **metastable**, nuclide is formed, which is identified by a lowercase letter *m* written after the mass number. ${}^{60m}\text{Co}$, for example, is produced by the electron emission of ${}^{60}\text{Fe}$.

$$ {}^{60}_{26}\text{Fe} \rightarrow {}^{60m}_{27}\text{Co} + {}^{0}_{-1}e $$

The metastable ${}^{60m}\text{Co}$ nuclide has a half-life of 10.5 min. Since gamma radiation carries neither charge nor mass, the product of γ-ray emission by ${}^{60m}\text{Co}$ is ${}^{60}\text{Co}$.

$$ {}^{60m}_{27}\text{Co} \rightarrow {}^{60}_{27}\text{Co} + \gamma \quad (\gamma\text{-ray emission}) $$

Spontaneous Fission

Nuclides with atomic numbers of 90 or more undergo a form of radioactive decay known as **spontaneous fission** in which the parent nucleus splits into a pair of smaller nuclei. The reaction is usually accompanied by the ejection of one or more neutrons.

$$ {}^{252}_{98}\text{Cf} \rightarrow {}^{140}_{54}\text{Xe} + {}^{108}_{44}\text{Ru} + 4\,{}^{1}_{0}n $$

For all but the very heaviest isotopes, spontaneous fission is a very slow reaction. Spontaneous fission of ${}^{238}\text{U}$, for example, is almost 2 million times slower than the rate at which this nuclide undergoes α-decay.

Solved Example 14-6

Predict the products of the following nuclear reactions.

(a) Electron emission by ${}^{14}\text{C}$
(b) Positron emission by ${}^{8}\text{B}$
(c) Electron capture by ${}^{125}\text{I}$
(d) Alpha emission by ${}^{210}\text{Rn}$
(e) Gamma-ray emission by ${}^{56\text{m}}\text{Ni}$

Solution

We can predict the product of each reaction by writing an equation in which both mass number and charge are conserved.

(a) ${}^{14}_{6}\text{C} \rightarrow {}^{14}_{7}\text{N} + {}^{0}_{-1}e$

(b) ${}^{8}_{5}\text{B} \rightarrow {}^{8}_{4}\text{Be} + {}^{0}_{+1}e$

(c) ${}^{125}_{53}\text{I} + {}^{0}_{-1}e \rightarrow {}^{125}_{52}\text{Te} + h\nu$

(d) ${}^{210}_{86}\text{Rn} \rightarrow {}^{206}_{84}\text{Po} + {}^{4}_{2}\text{He}$

(e) ${}^{56\text{m}}_{28}\text{Ni} \rightarrow {}^{56}_{28}\text{Ni} + \gamma$

Solved Example 14-7

$^{234}_{90}$Th disintegrates to give $^{206}_{82}$Pb as the final product. How many α- and β-particles are emitted during the process?

Solution

The reaction involved is $^{234}_{90}\text{Th} \rightarrow {}^{206}_{822}\text{Pb} + 7\,{}^{4}_{2}\text{He} + 6\,{}^{0}_{-1}e$. There are 7 α-particles and 6 β-particles.

Solved Example 14-8

Predict a reasonable decay mode for each of the following. Write the decay reaction and explain your reasoning:

(a) ^{243}Am **(b)** ^{17}F **(c)** ^{49}Ca **(d)** ^{181}Ir

Solution

(a) ^{243}Am: A very large nuclei, so α-decay is predicted. $^{243}_{95}\text{Am} \rightarrow {}^{4}_{2}\alpha + {}^{239}_{93}\text{Np}$

(b) ^{17}F: Fluoride's average molecular weight is 19, so this atom is light on neutron. A positron decay is predicted because it is rather light for an electron capture. $^{17}_{9}\text{F} \rightarrow {}^{0}_{+1}e + \nu + {}^{17}_{8}\text{O}$

(c) ^{49}Ca: Calcium average molecular weight is 40, so as a lighter element, it undergoes negatron decay. $^{49}_{20}\text{Ca} \rightarrow {}^{0}_{-1}e + {}^{48}_{21}\text{Sc} + \bar{\nu}$

(d) ^{181}Ir: Iridium's average molecular weight is 192. As a heavier element, it is more likely to undergo electron capture than positron decay. $^{181}_{77}\text{Ir} + {}^{0}_{-1}e \rightarrow {}^{181}_{76}\text{Os} + \nu$

Solved Example 14-9

^{214}Bi decays to isotope A by α-emission; A then decays to B by β-emission, which decays to C by another β-emission. Element C decays to D by still another β-emission, and D decays by α-emission to a stable isotope, E. What is the proper symbol of element E?

Solution

$$^{214}_{83}\text{Bi} \rightarrow {}^{4}_{2}\text{He} + \underset{(\text{A})}{^{210}_{81}\text{Tl}} \rightarrow {}^{0}_{-1}e + \underset{(\text{B})}{^{210}_{82}\text{Pb}} \rightarrow {}^{0}_{-1}e + \underset{(\text{C})}{^{210}_{83}\text{Bi}} \rightarrow {}^{0}_{-1}e + \underset{(\text{D})}{^{210}_{84}\text{Po}}$$

$$\underset{(\text{D})}{^{210}_{84}\text{Po}} \rightarrow {}^{4}_{2}\text{He} + \underset{(\text{E})}{^{206}_{82}\text{Pb}}$$

14.5 | DECAY MECHANISM IN NEUTRON-RICH AND NEUTRON-POOR NUCLIDES

In 1934 Enrico Fermi proposed a theory that explained the three forms of β-decay. He argued that a neutron could decay to form a proton by emitting an electron.

$$^{1}_{0}n \rightarrow {}^{1}_{1}\text{H} + {}^{0}_{-1}e \quad [\text{electron } (\beta^-) \text{ emission}]$$

A proton, on the other hand, could be transformed into a neutron by two pathways. It can capture an electron.

$$^{1}_{1}\text{H} + {}^{0}_{-1}e \rightarrow {}^{1}_{0}n \ (\text{electron capture})$$

or it can emit a positron

$$^{1}_{1}\text{H} \rightarrow {}^{1}_{0}n + {}^{0}_{+1}e \quad [\text{positron } (\beta^+) \text{ emission}]$$

Electron emission, therefore, leads to an *increase* in the atomic number of the nucleus.

$$^{14}_{6}\text{C} \rightarrow {}^{14}_{7}\text{N} + {}^{0}_{-1}e$$

Both electron capture and positron emission, on the other hand, result in a *decrease* in the atomic number of the nucleus.

$$^{7}_{4}\text{Be} + {}^{0}_{-1}e \rightarrow {}^{7}_{3}\text{Li} + h\nu$$

$$^{11}_{6}\text{C} \rightarrow {}^{11}_{5}\text{B} + {}^{0}_{+1}e + \nu$$

A plot of the number of neutrons vs. the number of protons for all of the stable naturally occurring isotopes is shown in Fig. 14.4. Several conclusions can be drawn from this plot.

1. The stable nuclides lie in a very narrow band of neutron-to-proton ratios.
2. The ratio of neutrons to protons in stable nuclides gradually increases as the number of protons in the nucleus increases.
3. Light nuclides, such as ^{12}C, contain about the same number of neutrons and protons. Heavy nuclides, such as ^{238}U, contain up to 1.6 times as many neutrons as protons.
4. The solid line represents a neutron-to-proton ratio of 1:1. There are no stable nuclides with atomic numbers larger than 83.
   - **(a)** Nuclei that lie above this line have too many neutrons and are therefore **neutron-rich**.
   - **(b)** Nuclei that lie below this line do not have enough neutrons and are therefore **neutron-poor**.

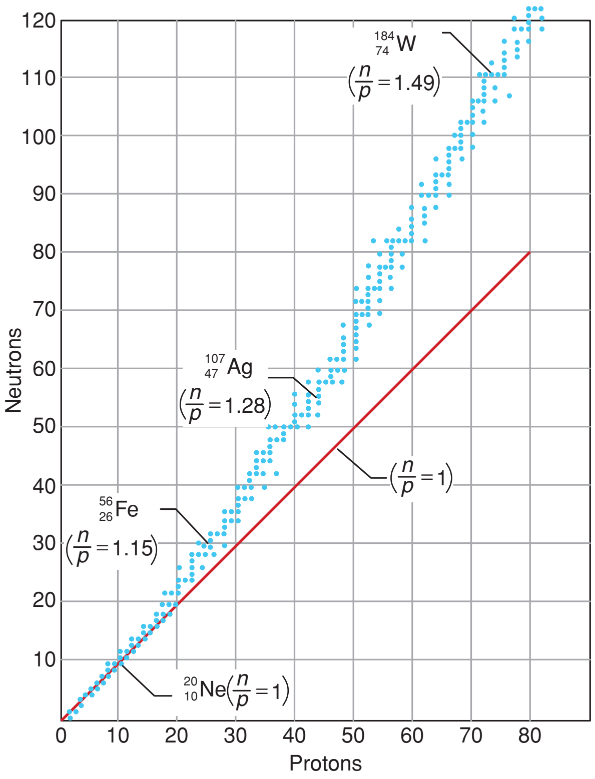


Figure 14.4 A graph of the number of neutrons vs. the number of protons for all stable naturally occurring nuclei.

The most likely mode of decay for a neutron-rich nucleus is one that converts a neutron into a proton. Every *neutron-rich* radioactive isotope with an atomic number smaller than 83 decays by electron (β^-) emission. ^{14}C, ^{32}P and ^{35}S, for example, are all neutron-rich nuclei that decay by the emission of an electron.

$$^{35}_{16}S \rightarrow {}^{35}_{17}Cl + {}^{0}_{-1}e \quad (\beta^- \text{emission})$$

Neutron-poor nuclides decay by modes that convert a proton into a neutron. Neutron-poor nuclides with atomic numbers less than 83 tend to decay by either electron capture or positron emission. Many of these nuclides decay by both routes, but positron emission is more often observed in the lighter nuclides, such as ^{22}Na.

$$^{22}_{11}Na \rightarrow {}^{22}_{10}Ne + {}^{0}_{+1}e \quad (\beta^+ \text{ emission})$$

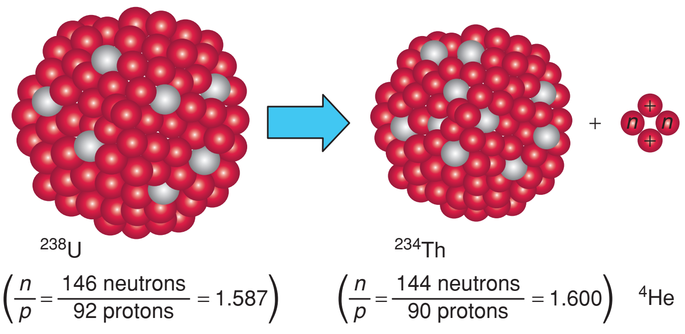
Electron capture is more common among heavier nuclides, such as ^{125}I, because the 1*s* electrons are held closer to the nucleus of an atom as the charge on the nucleus increases.

$$^{125}_{53}I + {}^{0}_{-1}e \rightarrow {}^{125}_{53}Te + h\nu \quad (\text{electron capture})$$

A third mode of decay is observed in *neutron-poor* nuclides that have atomic numbers larger than 83. Although it is not obvious at first, α-decay increases the ratio of neutrons to protons. Consider what happens during the α-decay of ^{238}U, for example.

$$^{238}_{92}U \rightarrow {}^{234}_{90}Th + {}^{4}_{2}He \quad (\alpha\text{-decay})$$

The parent nuclide (^{238}U) in this reaction has 92 protons and 146 neutrons, which means that the neutron-to-proton ratio is 1.587. The daughter nuclide (^{234}Th) has 90 protons and 144 neutrons, so its neutron-to-proton ratio is 1.600. The daughter nuclide is therefore slightly less likely to be neutron-poor as shown in Fig. 14.5.



+
n
n
+
+
^{238}U
$\left(\frac{n}{p}=\frac{146 \text{ neutrons}}{92 \text{ protons}}=1.587\right)$
^{234}Th
$\left(\frac{n}{p}=\frac{144 \text{ neutrons}}{90 \text{ protons}}=1.600\right)$
^{4}He

Figure 14.5 α-particle decay in neutron-poor nuclides such as ^{238}U.

Solved Example 14-10

Write the nuclear reactions for the following:

(a) the α-decay of ^{238}Pu,

(b) the negatron (negative β-particle) decay of ^{60}Co,

(c) the positron decay of ^{11}C,

(d) the electron capture decay of ^{208}Bi,

(e) the neutron-induced fission of ^{235}U into ^{144}Ba, ^{90}Kr and two neutrons,

(f) $^{238}\mathrm{U}(^{12}\mathrm{C}, 4n)^{246}\mathrm{Cf}$,

(g) $^{238}\mathrm{U}(n, \gamma)^{239}\mathrm{U}$.

Solution

(a) $^{238}_{94}\mathrm{Pu} \to {}^{4}_{2}\mathrm{He} + {}^{234}_{92}\mathrm{U}$

(b) $^{60}_{27}\mathrm{Co} \to {}^{0}_{-1}e + \bar{\nu} + {}^{60}_{28}\mathrm{Ni}$

(c) $^{11}_{6}\mathrm{C} \to {}^{0}_{+1}e + \bar{\nu} + {}^{11}_{5}\mathrm{B}$

(d) $^{208}_{83}\mathrm{Bi} + {}^{0}_{-1}e \to \bar{\nu} + {}^{208}_{82}\mathrm{Pb}$

(e) $^{235}_{92}\mathrm{U} + {}^{1}_{0}n \to {}^{144}_{56}\mathrm{Ba} + 2\,{}^{1}_{0}n + {}^{90}_{36}\mathrm{Kr}$

(f) $^{238}_{92}\mathrm{U} + {}^{12}_{6}\mathrm{C} \to 4\,{}^{1}_{0}n + {}^{246}_{98}\mathrm{Cf}$

(g) $^{238}_{91}\mathrm{U} + {}^{1}_{0}n \to {}^{239}_{92}\mathrm{U} + \gamma$

Solved Example 14-11

Predict the most likely modes of decay and the products of decay of the following nuclides: **(a)** ^{17}F, **(b)** ^{105}Ag and **(c)** ^{185}Ta.

Solution

The first step in predicting the mode of decay of a nuclide is to decide whether the nuclide is neutron-rich or neutron-poor. This can be done by comparing the mass number of the nuclide with the atomic weight of the element.

(a) The atomic weight of fluorine is 18.998 amu. Because the mass of an ^{17}F nuclide is *smaller* than that of the average fluorine atom, the ^{17}F nuclide must contain fewer neutrons. It is therefore likely to be *neutron-poor*. Because it is a relatively light nuclide, ^{17}F might be expected to decay by positron emission.

$$^{17}_{9}\mathrm{F} \to {}^{17}_{8}\mathrm{O} + {}^{0}_{+1}e \quad (\beta^{+}\text{emission})$$

(b) The atomic weight of silver is 107.868 amu. Because the mass of the ^{105}Ag nuclide is *smaller* than that of the average silver atom, it contains fewer neutrons than the stable isotopes of silver. ^{105}Ag is therefore likely to behave as a *neutron-poor* nuclide. Since ^{105}Ag is a relatively heavy nuclide, we might expect it to decay by electron capture.

$$^{105}_{47}\mathrm{Ag} + {}^{0}_{-1}e \to {}^{105}_{46}\mathrm{Pd} + h\nu \quad (\text{electron capture})$$

(c) The atomic weight of tantalum is 180.948 amu. The mass of the ^{185}Ta isotope is therefore significantly *larger* than that of the average tantalum atom, which means it contains an unusually large number of neutrons. Because this isotope is *neutron-rich*, it decays by electron emission.

$$^{185}_{73}\mathrm{Ta} \to {}^{185}_{74}\mathrm{W} + {}^{0}_{-1}e \quad (\beta^{-}\text{emission})$$

Solved Example 14-12

$^{27}_{13}$Al is a stable isotope. $^{29}_{13}$Al is expected to disintegrate by which emission?

Solution

Since $^{29}_{13}$Al has two neutrons more than required for stability, and is a neutron-rich nuclide, it will undergo β-emission.

Solved Example 14-13

Classify the following nuclides as stable, β-particle emitters and positron emitters:

$$^{195}_{80}\mathrm{Hg},\ {}^{208}_{82}\mathrm{Pb},\ {}^{8}_{5}\mathrm{B},\ {}^{150}_{67}\mathrm{Ho},\ {}^{30}_{13}\mathrm{Al},\ {}^{120}_{50}\mathrm{Sn} \text{ and } {}^{94}_{36}\mathrm{Kr}$$

Solution

Nuclides near the stability curve are probably stable:

$$^{208}_{82}\mathrm{Pb} \text{ and } {}^{120}_{50}\mathrm{Sn}$$

Those above the curve are negatron emitters:

$$^{30}_{13}\mathrm{Al} \text{ and } {}^{94}_{36}\mathrm{Kr}$$

Those below the curve are positron emitters:

$$^{195}_{80}\mathrm{Hg},\ {}^{8}_{5}\mathrm{B} \text{ and } {}^{150}_{67}\mathrm{Ho}.$$

14.6 | BINDING ENERGY AND NUCLEAR STABILITY

We should be able to predict the mass of an atom from the masses of the subatomic particles it contains. A helium atom, for example, contains two protons, two neutrons and two electrons. The mass of a helium atom therefore should be 4.0329802 amu.

$$\begin{aligned} 2(1.0072765)\ \text{amu} &= 2.0145530\ \text{amu} \\ 2(1.0086650)\ \text{amu} &= 2.0173300\ \text{amu} \\ 2(0.0005486)\ \text{amu} &= 0.0010972\ \text{amu} \\ \hline \text{Total mass} &= 4.0329802\ \text{amu} \end{aligned}$$

When the mass of a helium atom is measured, we find that the experimental value is smaller than the predicted mass by 0.0303769 amu.

$$\begin{aligned} \text{Predicted mass} &= 4.0329802\ \text{amu} \\ \text{Observed mass} &= 4.0026033\ \text{amu} \\ \hline \text{Mass defect} &= 0.0303769\ \text{amu} \end{aligned}$$

The difference between the mass of an atom and the sum of the masses of its protons, neutrons and electrons is called the **mass defect**. The mass defect of an atom reflects the stability of the nucleus. It is equal to the energy released when the nucleus is formed from its protons and neutrons. The mass defect is therefore also known as the **binding energy** of the nucleus.

The **binding energy** serves the same function for nuclear reactions as $\Delta H°$ for a chemical reaction. It measures the difference between the stability of the products of the reaction and the starting materials. The larger the binding energy, the more stable the nucleus. The binding energy can also be viewed as the amount of energy it would take to rip the nucleus apart to form isolated neutrons and protons. It is therefore literally the energy that binds together the neutrons and protons in the nucleus.

The binding energy of a nuclide can be calculated from its mass defect with Einstein's equation that relates mass and energy.

$$E = mc^2 \tag{14.2}$$

To obtain the binding energy in units of joules, we must convert the mass defect from atomic mass units into kilograms.

$$0.0303769\,\text{amu} \times \frac{1.6605655 \times 10^{-24}\,\text{g}}{1\,\text{amu}} \times \frac{1\text{kg}}{1000\,\text{g}} = 5.04428 \times 10^{-29}\,\text{kg}$$

Multiplying the mass defect in kilograms by the square of the speed of light in units of meters per second gives binding energy for a single helium atom of 4.53357×10^{-12} J.

$$E = (5.04428 \times 10^{-29}\ \text{kg})\ (2.9979246 \times 108\ \text{ms}^{-1})^2 = 4.53357 \times 10^{-12}\ \text{J}$$

Multiplying the result of this calculation by the number of atoms in a mole gives a binding energy for helium of 2.730×10^{12} J mol^{-1}, or 2.730 billion kJ mol^{-1}.

$$\frac{4.53357 \times 10^{-12}\,\text{J}}{1\,\text{atom}} \times \frac{6.022 \times 10^{23}\ \text{atoms}}{1\,\text{mol}} = 2.730 \times 10^{12}\ \text{J}\,\text{mol}^{-1}$$

This calculation helps us understand the fascination of nuclear reactions. The energy released when natural gas is burned is about 800 kJ mol^{-1}. The synthesis of a mole of helium releases 3.4 million times as much energy.

Since most nuclear reactions are carried out on very small samples of material, the mole is not a reasonable basis for measurement. Binding energies are usually expressed in units of electron volts (eV) or million electron volts (MeV) per atom. The binding energy of helium is 28.3×10^6 eV atom^{-1} or 28.3 MeV atom^{-1}.

$$\frac{4.53357 \times 10^{-12}\,\text{J}}{1\,\text{atom}} \times \frac{1\ \text{eV}}{1.602 \times 10^{-19}\,\text{J}} = 28.3 \times 10^6\,\text{eV}\,\text{atom}^{-1}$$

Calculations of the binding energy can be simplified by using the following conversion factor between the mass defect in atomic mass units and the binding energy in million electron volts.

$$1 \text{ amu} = 931.5016 \text{ MeV}$$

Binding energies gradually increase with atomic number, although they tend to level off near the end of the periodic table. A more useful quantity is obtained by dividing the binding energy for a nuclide by the total number of protons and neutrons it contains. This quantity is known as the **binding energy per nucleon**.

The binding energy per nucleon ranges from about 7.5 to 8.8 MeV for most nuclei, as shown in Fig. 14.6. It reaches a maximum, however, at an atomic mass of about 60 amu. The largest binding energy per nucleon is observed for ^{56}Fe, which is the most stable nuclide in the periodic table. Nuclei lighter than ^{56}Fe can become more stable by fusing together; nuclei significantly heavier than ^{56}Fe can become more stable by splitting apart.

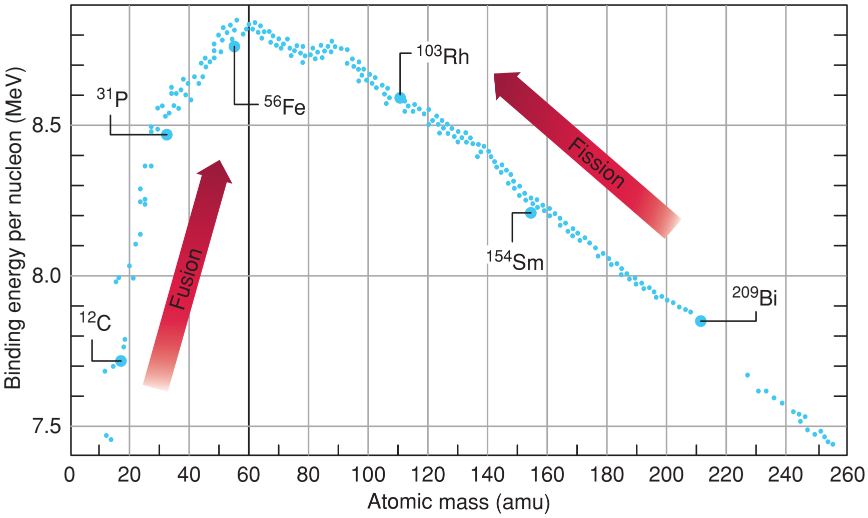


Figure 14.6 The binding energy per nucleon, reaches a maximum at ^{56}Fe.

The graph of binding energy per nucleon vs. atomic mass explains why energy is released when relatively small nuclei combine to form larger nuclei in **fusion reactions**.

$$^{12}_{6}\text{C} + {}^{12}_{6}\text{C} \xrightarrow{\text{Fusion}} {}^{24}_{12}\text{Mg}$$

It also explains why energy is released when relatively heavy nuclei split apart in **fission** (literally, "to split or cleave") **reactions**.

$$^{235}_{92}\text{U} \xrightarrow{\text{Fission}} {}^{139}_{56}\text{Ba} + {}^{94}_{36}\text{Kr} + 2{}^{1}_{0}n$$

There are a number of small irregularities in the binding energy curve at the low end of the mass spectrum, as shown in Fig. 14.7. The ^{4}He nucleus, for example, is much more stable than its nearest neighbors. The unusual stability of the ^{4}He nucleus explains why α-particle decay is usually much faster than the spontaneous fission of a nuclide into two large fragments.

$$\text{Packing fraction} = \frac{(\text{Isotopic mass} - \text{Mass number}) \times 10^4}{\text{Mass number}}$$

1. Its value may be negative, zero or positive.
2. Nuclei with positive packing fraction are highly unstable.
3. Packing fraction is least for H and maximum for Fe.

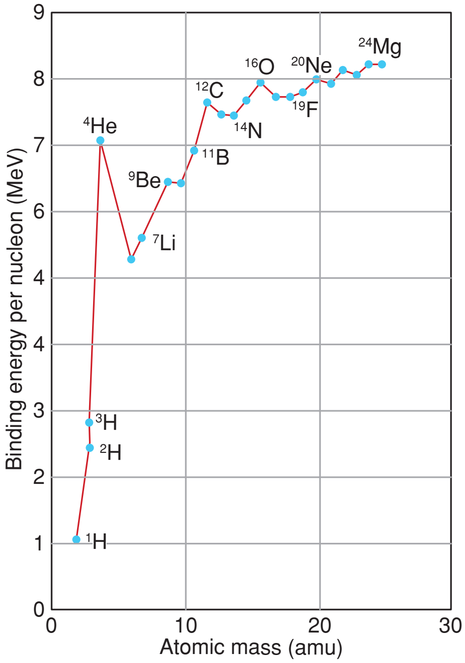


Figure 14.7 The binding energy per nucleon for most stable nuclei is between 7.8 and 8.8 meV per nucleon.

Solved Example 14-14

Calculate the binding energy of ^{235}U if the mass of this nuclide is 235.0439 amu.

Solution

A neutral ^{235}U atom contains 92 protons, 92 electrons, and 143 neutrons. The predicted mass of a ^{235}U atom is therefore, 236.9601 amu.

$$\begin{aligned} 92(1.00728)\text{ amu} &= 92.6698\text{ amu} \\ 92(0.0005486)\text{ amu} &= 0.0505\text{ amu} \\ 143(1.00867)\text{ amu} &= 144.2398\text{ amu} \\ \hline \text{Total mass} &= 236.9601\text{ amu} \end{aligned}$$

To calculate the mass defect for this nucleus, we subtract the observed mass from the predicted mass.

$$\begin{aligned} \text{Predicted mass} &= 236.9601\text{ amu} \\ \text{Observed mass} &= 235.0439\text{ amu} \\ \hline \text{Mass defect} &= 1.9162\text{ amu} \end{aligned}$$

Using the conversion factor that relates the binding energy to the mass defect, we obtain binding energy for ^{235}U as

$$\frac{1.9162\,\text{amu}}{1\,\text{atom}} \times \frac{931.50\text{ MeV}}{1\,\text{amu}} = 1784.9\text{ MeVatom}^{-1}$$

Solved Example 14-15

Calculate the binding energy per nucleon (in MeV) in He atom, $^{4}_{2}$He which has a mass of 4.001505 amu. Mass of one neutron = 1.008665 amu and mass of 1 hydrogen atom = 1.007825 amu.

Solution

He atom has 4 nucleons (2 protons + 2 neutrons). The mass of 2 protons and 2 neutrons add up to a total mass of 4.03188 u, however, the given mass is 4.001505 u. The mass defect is, therefore, 0.03038 u. From the expression $E = \Delta mc^2$, the binding energy for He is 0.03038 × 931.7 = 28.3 MeV. So, the average binding energy per nucleon is 28.3 MeV/4 = 7.07 MeV.

Solved Example 14-16

Calculate the binding energy (in MeV and J mol^{-1}) and binding energy per nucleon for ^{136}Xe (135.9072 daltons), ^{208}Pb (207.9766 daltons) and ^{28}Si (27.97693 daltons). Which nucleus is the most stable?

Solution

We know that mass of neutron = 1.0086641 and mass of proton + mass of electron = 1.008374
Also, 1 dalton = 931.7 MeV.
For ^{136}Xe: number of protons = number of electrons = 54 and number of neutrons = 82, so predicted mass = 137.16265 – 135.9072 dalton. Hence, mass defect is

Δm = 1.2555 daltons = 1169.7 MeV, so binding energy per nucleon = 1169.71136 = 8.601 MeV nucleon^{-1}
For ^{208}Pb: number of protons = electrons = 82, and number of neutrons = 126, so predicted mass = 209.77834 dalton. Hence, mass defect is 209.77834 – 207.97<< or

Δm = 1.8017 daltons = 1678.7 MeV. So binding energy per nucleon = 1678.7/208 = 8.071 MeV nucleon^{-1}

For ^{28}Si: number of protons = electrons = 14, and number of neutrons = 14, so predicted mass = 28.23853 daltons. Hence, mass defect is 28.23853 – 27.97<93, or

Δm = 0.26160 daltons = 243.73 MeV. So binding energy per nucleon = 243.73/28 = 8.705 MeV nucleon^{-1}

Therefore silicon-28 is the most stable nucleus.

14.7 | THE KINETICS OF RADIOACTIVE DECAY

Radioactive Nuclei Decay by First-Order Kinetics

Consider a radioactive substance A undergoing radioactive decay to form substance B, then if the initial concentration of the radioactive substance is N and the amount dN disintegrates in time t, then by first order kinetics

$$\text{Rate} = -\frac{\mathrm{d}N}{\mathrm{d}t} = kN$$

The rate of radioactive decay is therefore the product of a rate constant (k) times the number of atoms of the isotope in the sample (N). The negative sign shows that the number of isotopes of the atom decrease with increases in time. The rate of radioactive decay does not depend on the chemical state of the isotope. The rate of decay of ^{238}U, for example, is the same in uranium metal, uranium hexafluoride or any other compound of this element.

For radioactive decay, the rate constant k is known as the disintegration or decay constant and is represented by λ.

$$\lambda = \frac{-\mathrm{d}N}{N}\,\mathrm{d}t \tag{14.3}$$

When time $t = 1$ s,
$$\lambda = \frac{-\mathrm{d}N}{N}$$

Thus, disintegration constant can be defined as the fraction of the total number of atoms disintegrating per second. Integrating Eq. (14.3), we get

$$\ln N = \lambda t + A$$

where A is the integration constant. At $t = 0$, $N = N_0$, therefore, we have

$$\ln N = -\lambda t + \ln N_0 \Rightarrow \ln \frac{N_0}{N} = \lambda t \Rightarrow \frac{N_0}{N} = e^{\lambda t}$$

or
$$N = N_0 e^{-\lambda t} \Rightarrow N = N_0 10^{-\lambda t/2.303} \qquad (14.4)$$

The time required for decay of any specific fraction (n) of the isotope is proportional to the initial concentration:

$$t_{1/n} \propto [N_0]^0$$

The fraction of atoms (α) decayed in time t is given by

$$\alpha = \frac{N_0 - N}{N_0} = 1 - \frac{N}{N_0} = 1 - e^{-\lambda t} \qquad (14.5)$$

Half-Life Period

In our discussion of the kinetics of chemical reactions, we noted that the half-life of a first-order process is inversely proportional to the rate constant for this process.

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.6931}{k}$$

For radioactive processes, the rate constant k is replaced with disintegration constant λ. Both k and λ have the same units.

The **half-life** for the decay of a radioactive nuclide is the length of time it takes for exactly half of the nuclei in the sample to decay.

$$t_{1/2} = \frac{\ln 2}{\lambda} = \frac{0.693}{\lambda} \qquad (14.6)$$

The half-life of a nuclide can be used to estimate the amount of a radioactive isotope left after a given number of half-lives. If the initial amount of radioactive substance is N_0, then the amount of radioactive substance decomposed and left after subsequent half-lives is given in Table 14.2.

Table 14.2 Relation between the number of half-lives and the amount of radioactive substances present and decomposed

Number of half-lives ($nt_{1/2}$)	Amount of radioactive substance initially present	Amount of radioactive substance decomposed
0	N_0	0
1	$\frac{1}{2}N_0 = \left(\frac{1}{2}\right)^1 N_0$	$1 - \frac{1}{2}N_0 = \frac{1}{2}N_0$
2	$\frac{1}{4}N_0 = \left(\frac{1}{2}\right)^2 N_0$	$1 - \frac{1}{4}N_0 = \frac{3}{4}N_0$
3	$\frac{1}{8}N_0 = \left(\frac{1}{2}\right)^3 N_0$	$1 - \frac{1}{8}N_0 = \frac{7}{8}N_0$
4	$\frac{1}{16}N_0 = \left(\frac{1}{2}\right)^4 N_0$	$1 - \frac{1}{16}N_0 = \frac{15}{16}N_0$
N	$\left(\frac{1}{2}\right)^n N_0$	$1 - \left(\frac{1}{2}\right)^n N_0$

Solved Example 14-17

Calculate the fraction of ^{14}C that remains in a sample after eight half-lives.

Solution

Half of the ^{14}C present initially decays during the first half-life, half of what is left decays during the second half-life, and so on. The ^{14}C left after eight half-lives is equal to one-half raised to the eighth power.

$$\left(\frac{1}{2}\right)^8 = 0.00391$$

Less than 0.4% of the original ^{14}C is left after eight half-lives.

Solved Example 14-18

The half-life for ^{222}Rn is 3.823 days. How long would it take for a sample of ^{222}Rn that weighs 0.750 g to decay to 0.100 g?

Solution

We can start by calculating the rate constant for this decay from the half-life reaction.

$$\lambda = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{3.823} = 0.1813 \text{ days}^{-1}$$

We then use the integrated form of the first-order rate law.

$$\ln\left[\frac{(N)}{(N_0)}\right] = -\lambda t$$

The ratio of the number of atoms that remain in the sample to the number of atoms present initially is the same as the ratio of grams at the end of the time period (0.100 g) to the number of grams present initially (0.750 g).

$$\ln\left[\frac{(0.100)}{(0.750)}\right] = (-0.1813 \text{ days}^{-1})t$$

Solving for t, we find that it takes 11.1 days for 0.750 g of ^{222}Rn to decay to 0.100 g of this nuclide.

Solved Example 14-19

You have 0.1 gram-atom of a radioactive isotope $^{A}_{Z}X$ (half-life = 5 days). How many number of atoms will decay during the eleventh day?

Solution

The number of atoms undergoing decay is $N_0 = 0.1 \times 6.023 \times 10^{23} = 6.023 \times 10^{22}$ atoms.

The number of atoms decayed after ten days $= \dfrac{6.023\times10^{22}}{2\times2} = 1.505\times10^{22}$

After 11 days, the number of atoms decayed $= N_0 e^{-\lambda t} = 6.023\times e^{-(0.693\times11)/5} = 6.023\times10^{22}\times0.2177 = 1.31\times10^{22}$

Hence, the number of atoms decayed on the eleventh day $= (1.505 - 1.31)\times10^{22} = 1.937\times10^{21}$

Solved Example 14-20

Calculate the half-life of $^{23}_{11}Na$ if 2.4×10^{-5} g sample disintegrates at the rate of 7.75×10^{12} atoms s^{-1}.

Solution

The disintegration constant,

$$\lambda = \frac{\text{Disintegration rate}}{\text{Number of atoms present}}.$$

The number of atoms of ^{24}Na present $= 2.4\times10^{-5}\times\dfrac{1}{24}\times6.023\times10^{23} = 6.023\times10^{17}$ and given that rate $= 7.75\times10^{12}$ atoms s^{-1}. On substituting, we get

$$\lambda = \frac{7.75\times10^{12}}{6.023\times10^{17}} = 1.286\times10^{-5}\text{ s}^{-1}$$

$$\text{Therefore, } t_{1/2} = \frac{0.693}{\lambda} = \frac{0.693}{1.286\times10^{-5}} = 0.5388\times10^{5}\text{ s}$$

Average Life

The atoms of radioactive substance disintegrate in a phased manner. Some atoms disintegrate early while other atoms disintegrate in later half-times. The average or mean life of an atom is thus the sum of lives of all atoms divided by the total number of atoms

$$\text{Average life } (\tau_{\text{avg}}) = \frac{\text{Total lifetime of all atoms}}{\text{Total number of atoms}} \tag{14.7}$$

Let the number of radioactive atoms in a sample initially be N_0 and at time t be N. If the number of atoms disintegrating between time $(t + \mathrm{d}t)$ is given by $\mathrm{d}N$, then, total life of $\mathrm{d}N$ atoms can be given by $\mathrm{d}N \times (t + \mathrm{d}t)$ or $\mathrm{d}N \times t$ (neglecting $\mathrm{d}t$ as it is very small). Therefore,

$$\text{Total life of all the atoms } = \int_0^{N_0} t\,\mathrm{d}N = \int_0^{\infty} t\,\mathrm{d}N \text{ (as number of initial number of atoms is very large)}$$

The average life of atom is thus given by

$$\tau_{\text{avg}} = \frac{\int_0^{\infty} t\,\mathrm{d}N}{N_0} = \frac{\int_0^{\infty} -t\lambda N \mathrm{d}t}{N_0} \quad \left(\text{as } -\frac{\mathrm{d}N}{\mathrm{d}t} = \lambda N\right)$$

$$= \frac{\int_0^{\infty} -t\lambda N_0 e^{-\lambda t} \mathrm{d}t}{N_0} \quad (\text{as } N = N_0 e^{-\lambda t})$$

$$= \int_0^{\infty} -t\lambda e^{-\lambda t} \mathrm{d}t = \frac{1}{\lambda}$$

The average life is thus equal to the reciprocal of the decay constant. Using this relation in expression for half-life, we get

$$t_{1/2} = \frac{0.693}{\lambda} = 0.693 \times \tau_{\text{avg}} \Rightarrow \tau_{\text{avg}} = 1.44 t_{1/2} \tag{14.8}$$

If $t = 1/\lambda$, then

$$N = N_0 e^{-\lambda t} = N_0 e^{-1} = 0.37 N_0$$

Thus when the time is equal to the reciprocal of decay constant, 63% of the substance undergoes disintegration. Since reciprocal to disintegration constant is also equal to τ_{avg}, **average life can be defined as the time during which about 63% of the substance undergoes disintegration**.

Solved Example 14-21

If half-life of Ra is 1580 years, then calculate its average life.

Solution

$$\tau_{\text{avg}} = 1.44 t_{1/2} = 1.44 \times 1580 = 2.275 \times 10^3 \text{ years}$$

14.8 | RADIOACTIVE EQUILIBRIUM

The radioactive decay can take place in steps, wherein the radioactive substance decays to a radioactive intermediate (daughter nuclei) which further disintegrates to the stable product.

$$\underset{\substack{\text{Radioactive}\\ \text{element}}}{\text{A}} \rightarrow \underset{\substack{\text{Daughter}\\ \text{nuclei}}}{\text{B}} \rightarrow \underset{\substack{\text{Stable}\\ \text{element}}}{\text{C}}$$

When the rate of decay of radioactive substance A to form element B is same as the rate of formation of product C from B, the system is said to be in **radioactive equilibrium**.

If λ_1 and λ_2 are the disintegration constants for the two reactions and N_1 and N_2 is the number of atoms present for A and B at time t, then the rate of formation of B or decay of A is given by $\lambda_1 N_1$ and rate of disintegration of B is given by $\lambda_2 N_2$. At equilibrium,

$$\lambda_1 N_1 = \lambda_2 N_2$$

or
$$\frac{N_1}{N_2} = \frac{\lambda_2}{\lambda_1} = \frac{1/\lambda_1}{1/\lambda_2} = \frac{(\tau_{\text{avg}})_1}{(\tau_{\text{avg}})_2} \tag{14.9}$$

Thus, the number of atoms of A and B are in the ratio of their average life times.
We know that $t_{1/2} = 0.693/\lambda$. Substituting in equilibrium relation, we have

$$\frac{N_1}{N_2} = \frac{(t_{1/2})_1}{(t_{1/2})_2} \tag{14.10}$$

Let us consider two cases:

Case 1: When $\lambda_1 < \lambda_2$ and $(t_{1/2})_1 \lgroup (t_{1/2})_2$

This case implies that the parent element has longer life than the daughter element, but half-lives of both are nearly the same. The number of parent nuclei at any time t is given by

$$N_1 = N_0 e^{-\lambda_1 t}$$

The amount of daughter element formed at any time t can be calculated using the relation

$$N_2 = \frac{N_0 \lambda_1}{\lambda_2 - \lambda_1}[e^{-\lambda_1 t} - e^{-\lambda_2 t}] \tag{14.11}$$

When t is sufficiently large, $e^{-\lambda_2 t} \ll e^{-\lambda_1 t}$, so the number of daughter nuclei being formed at any time t is

$$N_2 = \frac{\lambda_1}{\lambda_2 - \lambda_1} \cdot N_0 e^{-\lambda_1 t} = \frac{\lambda_1}{\lambda_2 - \lambda_1} \cdot N_1$$

Therefore,
$$\frac{N_1}{N_2} = \frac{\lambda_2 - \lambda_1}{\lambda_1} \tag{14.12}$$

The time at which maximum activity of the daughter element is observed can be calculated using the relation

$$t_{\max} = \frac{2.303}{\lambda_2 - \lambda_1} \log_{10}\left(\frac{\lambda_2}{\lambda_1}\right) \tag{14.13}$$

This condition is called **transient equilibrium** and Eq. (14.12) is a steady state where the ratio of the parent and daughter element becomes constant.

Case 2: When $\lambda_1 > \lambda_2$ and $(t_{1/2})_1 < (t_{1/2})_2$

When the parent element has shorter half-life than the daughter element, steady state is not achieved.

Parallel Decay

We have seen that the radioactive decay process though irreversible can reach equilibrium between disintegrating parent and daughter nuclei. Let us now examine the case when a parent element disintegrates through two parallel paths illustrated as

$$\begin{tikzcd} \text{A} \arrow[r] \arrow[d] & \text{B} \\ \text{C} & \end{tikzcd}$$

If the rate of disintegration of A to B is given by λ_1 and that of A to C is given by λ_2, then the total rate of disintegration of A is

$$\lambda = \lambda_1 + \lambda_2 \tag{14.14}$$

Here the decay constants for each process can be expressed as

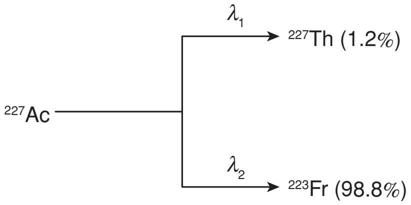
$$\begin{aligned} \lambda_1 &= [\text{Fractional yield of B}] \times \lambda \\ \lambda_2 &= [\text{Fractional yield of C}] \times \lambda \end{aligned} \tag{14.15}$$

Solved Example 14-22

^{227}Ac has a half-life of 21.8 years with respect to radioactive decay. The decay follows two parallel paths, one leading to ^{227}Th and the other leading to ^{223}Fr. The percentage yields of these two daughter nuclides are 1.2% and 98.8%, respectively. What is the rate constant in years^{-1}, for each of the separate paths?

Solution

λ_{Ac} is equal to the sum of λ_1 and λ_2.



We have $\lambda_{\text{Ac}} = \dfrac{0.693}{21.8} = 0.0318$ per year

Thus, we have $\lambda_1 + \lambda_2 = 0.0318$. Also, $\lambda_1/\lambda_2 = 98.8/1.2 = 82.33$

Hence, we have

$$82.33\lambda_2 + \lambda_2 = 0.0318 \Rightarrow \lambda_2 = \frac{0.0318}{83.33} = 3.82 \times 10^{-4}$$

and $\lambda_1 = 82.33 \times 3.82 \times 10^{-4} = 3.14 \times 10^{-2}$

Solved Example 14-23

Consider

$$^{228}\text{Th} \xrightarrow{-\alpha} {}^{224}\text{Ra} \xrightarrow{-\alpha} {}^{220}\text{Rn}$$

where $t_{1/2}$ (^{228}Th) = 1.913 years, $t_{1/2}$ (^{224}Ra) = 3.64 days. Determine the $N_{\text{Th}}/N_{\text{Ra}}$ ratio once transient equilibrium has been established in which $t_{1/2}$ (parent) > $t_{1/2}$ (daughter) or λ (parent) < λ (daughter).

Solution

At transient equilibrium, we have

$$\frac{N_{\text{Th}}}{N_{\text{Ra}}} = \frac{\lambda_{\text{Ra}} - \lambda_{\text{Th}}}{\lambda_{\text{Th}}} \approx \frac{\lambda_{\text{Ra}}}{\lambda_{\text{Th}}} = \frac{(t_{1/2})_{\text{Th}}}{(t_{1/2})_{\text{Ra}}} = \frac{1.913\ \text{years}}{(3.64/365)\ \text{years}} = 192$$

Solved Example 14-24

If $t_{1/2}$ of A is 12 h and that of B is 60 min in the radioactive equilibrium A → B, then calculate the time at which B will have maximum activity.

Solution

We know that $\quad t_{\max} = \dfrac{2.303}{\lambda_{\text{B}} - \lambda_{\text{A}}} \log\left(\dfrac{\lambda_{\text{B}}}{\lambda_{\text{A}}}\right)$

where

$$\lambda_{\text{A}} = \frac{0.693}{12} = 0.058\ \text{h}^{-1} \text{ and } \lambda_{\text{B}} = \frac{0.693}{60/60} = 0.693\ \text{h}^{-1}$$

Substituting, we get

$$t_{\max} = \frac{2.303}{0.058 - 0.693} \log\left(\frac{0.058}{0.693}\right) = \frac{2.303}{-0.635} \log(0.0836) = 3.91\ \text{h}$$

14.9 | ACTIVITY OF RADIOACTIVE SUBSTANCES, DETECTION AND UNITS OF RADIOACTIVITY

The rate at which a radioactive isotope decays is called the **activity** (A) of the isotope. It is measured as the number of disintegrations taking place per second. The activity per kilogram (sometimes gram is also used) of a radioactive substance is known as *specific activity*. A substance with higher activity will disintegrate faster and *vice versa*. The relative rates at which radioactive nuclei decay can be expressed in terms of either the rate constants for the decay or the half-lives of the nuclei. We can conclude that ^{14}C decays more rapidly than ^{238}U, for example, by noting that the rate constant for the decay of ^{14}C is much *larger* than that for ^{238}U. We can reach the same conclusion by noting that the half-life for the decay of ^{14}C is much *shorter* than that for ^{235}U.

Detection of Radioactivity

The Geiger–Müller tube, one part of a **Geiger counter**, detects β- and γ-radiations having energy high enough to penetrate the tube's window. Inside the tube is a gas under low pressure in which ions form when radiation enters. The ions permit a pulse of electricity to flow, which activates a current amplifier, a pulse counter, and an audible click. A **scintillation counter** contains a sensor composed of a substance called a **phosphor** that emits a tiny flash of light when struck by a particle of ionizing radiation. These flashes can be magnified electronically and automatically counted.

The rate at which a radioactive substance decays is measured by counting the number of particles emitted by a mass of substance per unit time. Two types of counters are mainly used for the purpose of detection and measurement of radiation and these are described as follows.

1. **Scintillation counter:** This is used mainly for the detection and measurement of g radiation. It consists of a scintillator or sensor composed of a substance called a phosphor which generates photon of light when struck by incident radiation. These flashes can be magnified electronically and automatically counted. The scintillator generally used are sodium iodide (NaI), thallium iodide (TlI) for detection of γ-radiation and cesium iodide (CsI) and zinc sulphide (ZnS) for detection of α-particles.
2. **Geiger Muller counter:** This is generally used for detection and measurement of charged particles, such as α- and β-particles which have high energy to penetrate the tube's window. An inert gas such as argon, helium or neon filled in the Geiger-Muller tube functions as a radiation detection medium. The particles of radiation ionize the inert gas at low pressure and the ionized gas particles are formed. The ions permit a pulse of electricity to flow, which activates a current amplifier, a pulse counter, and an audible click. For detection of neutrons boron trifluoride is mixed with the inert gas and a plastic moderator is used to slow down the neutrons. α-particles are created in the counter from the neutrons and they are hence counted.

Units of Radioactivity

The most common unit of activity is the **curie** (Ci), which was originally defined as the number of disintegrations per second in 1 g of ^{226}Ra. The curie is now defined as the amount of radioactive isotope necessary to achieve an activity of 3.700×10^{10} disintegrations per second. The curie is a very large unit of measurement. Activities of samples handled in the laboratory are therefore often reported in millicuries (mCi) = 10^{-3} Ci or microcuries (μCi) = 10^{-6} Ci. The unit of decay constant λ is time^{-1}.

Another unit used for measuring radioactivity is Rutherford (Rd) and it is defined as the amount of radioactive substance that undergoes 10^6 disintegrations per second. Smaller units like milli- and micro-Rutherford are also used and these correspond to the substance causing 10^3 or 1 disintegrations per second, respectively. Internationally, the S.I. unit of radioactivity being used now is **becquerel** (Bq), where

$$1 \text{ becquerel} = 1 \text{ radioactive decay per second} \tag{14.16}$$

$1 \text{ Ci} = 3.7 \times 10^{10} \text{ disintegrations s}^{-1} = 3.7 \times 10^{10} \text{ Bq}$

A liter of air has an activity of about 0.04 Bq, due to carbon-14 in its carbon dioxide. A gram of natural uranium has an activity of about 2.6×10^{-4} Bq. The becquerel is named after Henri Becquerel (1852–1908), the discoverer of radioactivity, who won a Nobel prize in 1903.

Nuclear radiation can have varying effects depending on the energy of the radiation and its ability to be absorbed. The unit **gray (Gy)** is the S.I. unit of *absorbed dose*, and 1 gray corresponds to 1 J of energy absorbed per kilogram of absorbing material. The unit **rad** is an older unit of absorbed dose, 1 rad being the absorption of 10^{-2} J kg^{-1} of tissue. Thus, 1 Gy equals 100 rad. Rad is generally multiplied by a factor called relative biological effectiveness (RBE) which is a measure of relative biological damage caused by the radiation.

The unit gray is not a good basis for comparing the biological effects of radiation in tissue, because these effects depend not just on the energy absorbed but also on the kind of radiation and the tissue itself. The unit **sievert (Sv)**, the S.I. unit of *dose equivalent*, was invented to meet this problem. The unit **rem** is an older unit of dose equivalent, one still used in medicine. Its value is generally taken to equal 10^{-2} Sv. *Rem* stands for roentgen equivalent for man, where the *roentgen* is a unit related to ionizing radiations, such as X-rays and γ-rays.

Solved Example 14-25

The most abundant isotope of uranium is ^{238}U. Analysis of uranium ore samples suggests that 99.276% of the atoms of uranium are ^{238}U. Calculate the activity of the ^{238}U in 1L of a 1.00 M solution of the uranyl ion, UO_2^{2+}. The rate constant for the decay of this isotope is 4.87×10^{-18} disintegrations per second.

Solution

The rate at which the ^{238}U isotope decays depends on the rate constant for this reaction (k) and the number of uranium atoms in the sample (N). The rate constant for the decay of this nuclide was given in the statement of the problem, and we can calculate the number of uranium atoms in the sample by noting that a liter of a 1.00 M UO_2^{2+} solution contains one mole of uranium atoms.

$$\text{Rate} = \lambda N = (4.87 \times 10^{-18}\ \text{s}^{-1})(6.10 \times 10^{23}\ \text{atoms}) = 2.93 \times 10^{6}\ \text{atoms s}^{-1}$$

To calculate the activity of this sample, we have to convert from disintegrations per second (atom s^{-1}) to curies.

$$2.93 \times 10^{6}\ \text{atoms s}^{-1} \times \frac{1\ \text{Ci}}{3.700 \times 10^{10}\ \text{atoms s}^{-1}} = 7.92 \times 10^{-5}\ \text{Ci}$$

This sample has an activity of 79.2 μCi.

Solved Example 14-26

Plutonium-238 has been used as a source to power heart pacemaker batteries. Its half-life is 87.74 years. Calculate the activity in units of curies for 0.25 g of pure plutonium-238 used in a pacemaker battery. Why is it a good power source in a pacemaker?

Solution

The half-life is

$$87.74\ \text{years} \times \left(\frac{365.25\ \text{day}}{1\ \text{year}}\right) \times \left(\frac{24\ \text{h}}{1\ \text{day}}\right) \times \left(\frac{60\ \text{min}}{1\ \text{h}}\right) \times \left(\frac{60\ \text{s}}{1\ \text{min}}\right)$$

$$= 2.769 \times 10^{9}\ \text{s}$$

The disintegration constant is

$$\lambda = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{2.769 \times 10^{9}\ \text{s}} = 2.503 \times 10^{-10}\ \text{s}^{-1}$$

$$\text{Now, } 0.25\ \text{g} \times \frac{1\ \text{mol}}{238\ \text{g}} \times \frac{(6.20 \times 10^{23}\ \text{atoms})}{1\ \text{mol}} = 6.3 \times 10^{20}\ \text{atoms}$$

So, activity $= \lambda N = 2.503 \times 10^{-10} \times 6.3 \times 10^{20} = 1.6 \times 10^{11}$ dps

In curie units, we have

$$1.6 \times 10^{11}\ \text{dps} \times \left(\frac{1\ \text{Ci}}{3.7 \times 10^{10}\ \text{dps}}\right) = 4.3\ \text{Ci}$$

Plutonium-238 satisfies all the conditions for a good pacemaker, which are as follows: **(a)** a very small amount of fuel is required; **(b)** as an α emitter it is easily shielded and **(c)** it lasts for a very long time.

Solved Example 14-27

A ^{60}Co source ($t_{1/2} = 5.2714$ years) that had an initial activity of 5.0 Ci has been in a laboratory for 15 years. Calculate the exposure rate at 3.0 ft from the source. Assume there is no shielding around the source and remember to account for decay of the source. The value of n is 1 for both the ^{60}Co γ-rays (which have energies of 1.3325 MeV and 1.1732 MeV) and the β-ray has energy of 0.338 MeV.

Solution

Converting $t_{1/2}$ in seconds, we get

$$5.2714\ \text{years} \times \left(\frac{365.25\ \text{day}}{1\ \text{year}}\right) \times \left(\frac{24\ \text{h}}{1\ \text{day}}\right) \times \left(\frac{3600\ \text{s}}{1\ \text{h}}\right)$$

$$= 1.664 \times 10^{8}\ \text{s}$$

$$A_0 = 5.0\ \text{Ci} \times \left(\frac{3.7 \times 10^{10}}{1\ \text{Ci}}\right) = 1.85 \times 10^{11}\ \text{dps}$$

But $A_0 = \lambda N_0 \Rightarrow 1.85 \times 10^{11} = (4.16 \times 10^{-9}) N_0$

or $N_0 = 4.44 \times 10^{19}$ atoms

Given that 15 years $= 4.73 \times 10^{8}$ s and 3.0 ft $= 91.4$ cm. Now,

$$\ln N_0 - \ln N = \lambda t$$

So, $\ln(4.44 \times 10^{19}) - \ln N = (4.16 \times 10^{-9}\ \text{s}^{-1}) \times (4.73 \times 10^{8}\ \text{s})$

or $N = 5.9 \times 10^{18}$

Now, $A = \lambda N = (4.16 \times 10^{-9})(5.9 \times 10^{18}) = 0.67$ Ci or 670 *mCi*

$$\beta_1 = \frac{338000 \times 670 \times 1}{(91.4)^2} = 2.7 \times 10^{4}\ \text{mrem h}^{-1}$$

$$\gamma_1 = \frac{6 \times 670 \times 1.3325 \times 1}{9} = 595\ \text{mrem h}^{-1}$$

$$\gamma_2 = \frac{6 \times 670 \times 1.1732 \times 1}{9} = 524\ \text{mrem h}^{-1}$$

Therefore, the total exposure rate $= 2.8 \times 10^{4}$ m rem h^{-1} = 24 rem h^{-1}.

Solved Example 14-28

The limit of a particular detection system is 0.002 dps for 1 g sample. Find the maximum half-life that this system could detect in a 1 g sample of a nuclide of mass number 200.

Solution

We know that the activity is $A = \left(\frac{0.693}{t_{1/2}}\right)N$. So, $t_{1/2}$ for activity of 0.002 dps is

$$t_{1/2} = \frac{0.693}{0.002} \times \frac{6.023 \times 10^{23}}{200} = 1.043 \times 10^{24}\ \text{s}$$

Solved Example 14-29

A mixture of ^{239}Pu and ^{240}Pu to have a specific activity of 6.0×10^9 dps. The half-lives of the isotopes are 2.44×10^4 and 6.58×10^3 years, respectively. Calculate the isotopic composition of this sample.

Solution

Specific activity is defined as the activity per gram of each isotope and is given by

$$A_{^{239}\text{Pu}} = \lambda N = \frac{0.693N}{t_{1/2}} = \frac{0.693 \times (6.023 \times 10^{23})}{2.44 \times 10^4 \times 239}$$
$$= 7.15 \times 10^{16}\ \text{years}^{-1}\text{g}^{-1} = 2.27 \times 10^9\ \text{s g}^{-1}$$

$$A_{^{240}\text{Pu}} = \lambda N = \frac{0.693N}{t_{1/2}} = \frac{0.693 \times (6.023 \times 10^{23})}{6.58 \times 10^3 \times 240}$$
$$= 2.64 \times 10^{17}\ \text{years}^{-1}\text{g}^{-1} = 8.37 \times 10^9\ \text{s g}^{-1}$$

Now, the given specific activity of mixture is $6{\cdot}0 \times 10^9$ dps^{-1}.

Suppose the fraction of ^{239}Pu in the mixture be x, then fraction of ^{240}Pu is $1 - x$. Now, we have

$$(2.27 \times 10^9)x + (1-x)(8.37 \times 10^9) = 6.0 \times 10^9$$
$$(2.27 - 8.37) \times 10^9\, x = (6.0 - 8.37) \times 10^9$$
$$6.1x = 2.37 \Rightarrow x = 0.39$$

So the isotopic composition is 39%.

14.10 | NATURAL VS. INDUCED RADIOACTIVITY

Natural Radioactivity

The vast majority of the nuclides found in nature are stable. If our planet is 4.6 billion years old, the only radioactive isotopes that should remain are members of three classes.

1. Isotopes with half-lives of at least 10^9 years, such as ^{238}U.
2. Daughter nuclides produced when long-lived radioactive nuclides decay, such as the ^{234}Th ($t_{1/2} = 24.1$ days) produced by the α-decay of ^{238}U.
3. Nuclides such as ^{14}C that are still being synthesized.

In Section 14.2, we encountered the factors that influence the stability of a nuclide:

1. Stability of even number of protons and neutron.
2. Stability of filled shells (magic number).
3. Ratio of neutrons to protons. (Nuclei that contain either too many or too few neutrons are unstable.)

If nuclei tend to be more stable when they have even numbers of protons and neutrons, it is not surprising that nuclides with an odd number of both protons and neutrons are unstable. ^{40}K is one of only five naturally occurring nuclides that contain both an odd number of protons and an odd number of neutrons. This nuclide simultaneously undergoes the electron capture and positron emission expected for neutron-poor nuclides and the electron emission observed with neutron-rich nuclides, as we saw in Fig. 14.4.

Only 18 radioactive isotopes with atomic numbers of 80 or less can be found in nature. With the exception of ^{14}C, which is continuously synthesized in the atmosphere, all these elements have lifetimes longer than 10^9 years. Although these isotopes all undergo radioactive decay, they decay so slowly that reasonable quantities are still present, 4.6 billion years after the planet was formed.

Radioactive Series

The parent nuclide is ^{232}Th, which undergoes α-decay to form ^{228}Ra. The product of this reaction decays by β-emission to form ^{228}Ac, which decays to ^{228}Th, and so on, until the stable ^{208}Pb isotope is formed. This family of radionuclides is called the **4*n* series**, because all its members have a mass number that can be divided by 4 (Fig. 14.8).

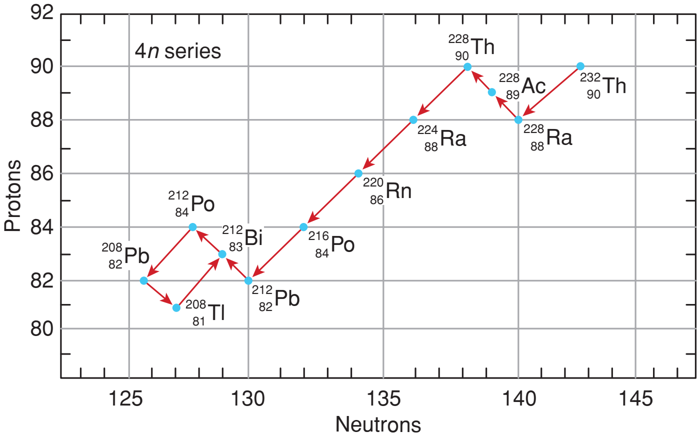


Figure 14.8 The 4*n* series starts with ^{232}Th and eventually decays to ^{208}Pb.

A second family of radioactive nuclei starts with ^{238}U and decays to form the stable ^{206}Pb isotope. Every member of this series has a mass number that fits the equation $4n + 2$. The third family, known as the $4n + 3$ series, starts with ^{235}U and decays to ^{207}Pb. A $4n + 1$ series once existed, which started with ^{237}Np and decayed to form the only stable isotope of bismuth, ^{209}Bi. The half-life of every member of this series is less than 2×10^6 years, however, so none of the nuclides produced by the decay of neptunium remain in detectable quantities on the earth.

The heavy radioactive elements may be grouped into four decay series. The common radioactive elements thorium, uranium and actinium occur naturally and belong to three different series named after them. They are the parent members of their respective series and have the longest half-life periods. They decay by a series of α- and β-emissions, and produce radioactive elements which are successively more stable until finally a stable isotope is reached. All three series terminate with lead ($^{206}_{82}$Pb, $^{207}_{82}$Pb and $^{202}_{82}$Pb). Following the discovery of the artificial post-uranium elements, the neptunium series has been added, which ends with bismuth, $^{209}_{93}$Bi.

1. Thorium (4*n*) series
2. Neptunium ($4n + 1$) series
3. Uranium ($4n + 2$) series
4. Actinium ($4n + 3$) series

The numbers in brackets indicate that the parent and all the members of a particular series have mass numbers exactly divisible by four, or divisible by four with a remainder of one, two or three. There is no natural cross-linking between the four series, although this can be performed artificially (Fig. 14.9).

Induced Radioactivity

In 1934, Irene Curie, the daughter of Pierre and Marie Curie, and her husband, Frederic Joliot, announced the first synthesis of an artificial radioactive isotope. They bombarded a thin piece of aluminum foil with α-particles produced by the decay of polonium and found that the aluminum target became radioactive. Chemical analysis showed that the product of this reaction was an isotope of phosphorus.

$$^{27}_{13}\mathrm{Al} + ^{4}_{2}\mathrm{He} \rightarrow ^{30}_{15}\mathrm{P} + ^{1}_{0}n$$

In the next 50 years, more than 2000 other artificial radionuclides were synthesized. The process by which a stable isotope is converted into radioactive element by artificial means (artificial transmutation) is called artificial or induced radioactivity.

A shorthand notation has been developed for nuclear reactions such as the reaction discovered by Curie and Joliot. The parent (or target) nuclide and the daughter nuclide are separated by parentheses that contain the symbols for the particle that hits the target and the particle or particles released in this reaction.

$$^{27}_{13}\mathrm{Al}(\alpha, n)^{30}_{15}\mathrm{P}$$

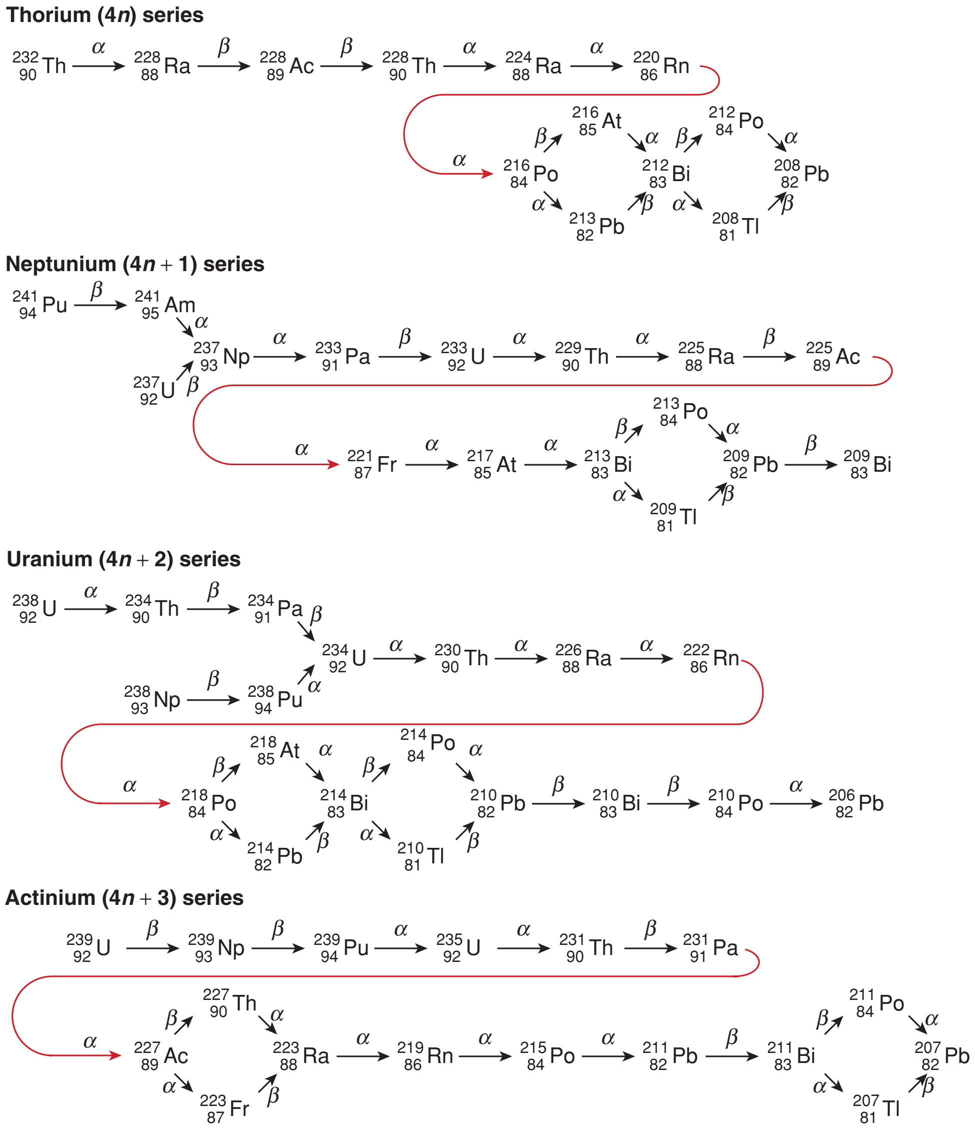

Thorium (4n) series
$^{232}_{90}$Th α $^{228}_{88}$Ra β $^{228}_{89}$Ac β $^{228}_{90}$Th α $^{224}_{88}$Ra α $^{220}_{86}$Rn
α $^{216}_{84}$Po β $^{216}_{85}$At α $^{212}_{83}$Bi β $^{212}_{84}$Po α $^{208}_{82}$Pb
α $^{213}_{82}$Pb β α $^{208}_{81}$Tl β
Neptunium (4n + 1) series
$^{241}_{94}$Pu β $^{241}_{95}$Am α
$^{237}_{92}$U β $^{237}_{93}$Np α $^{233}_{91}$Pa β $^{233}_{92}$U α $^{229}_{90}$Th α $^{225}_{88}$Ra β $^{225}_{89}$Ac
α $^{221}_{87}$Fr α $^{217}_{85}$At α $^{213}_{83}$Bi β $^{213}_{84}$Po α $^{209}_{82}$Pb β $^{209}_{83}$Bi
α $^{209}_{81}$Tl β
Uranium (4n + 2) series
$^{238}_{92}$U α $^{234}_{90}$Th β $^{234}_{91}$Pa β
$^{234}_{92}$U α $^{230}_{90}$Th α $^{226}_{88}$Ra α $^{222}_{86}$Rn
$^{238}_{93}$Np β $^{238}_{94}$Pu α
α $^{218}_{84}$Po β $^{218}_{85}$At α $^{214}_{83}$Bi β $^{214}_{84}$Po α $^{210}_{82}$Pb β $^{210}_{83}$Bi β $^{210}_{84}$Po α $^{206}_{82}$Pb
α $^{214}_{82}$Pb β α $^{210}_{81}$Tl β
Actinium (4n + 3) series
$^{239}_{92}$U β $^{239}_{93}$Np β $^{239}_{94}$Pu α $^{235}_{92}$U α $^{231}_{90}$Th β $^{231}_{91}$Pa
α $^{227}_{89}$Ac β $^{227}_{90}$Th α $^{223}_{88}$Ra α $^{219}_{86}$Rn α $^{215}_{84}$Po α $^{211}_{82}$Pb β $^{211}_{83}$Bi β $^{211}_{84}$Po α $^{207}_{82}$Pb
α $^{223}_{87}$Fr β α $^{207}_{81}$Tl β

Figure 14.9 Radioactivity series.

The nuclear reactions used to synthesize artificial radionuclides are characterized by enormous activation energies. Three devices are used to overcome these activation energies: linear accelerators, cyclotrons, and nuclear reactors. Linear accelerators or cyclotrons can be used to excite charged particles such as protons, electrons, α-particles, or even heavier ions, which are then focused on a stationary target. The following reaction, for example, can be induced by a cyclotron or linear accelerator.

$$^{24}_{12}\mathrm{Mg} + ^{2}_{1}\mathrm{H} \rightarrow ^{22}_{11}\mathrm{Na} + ^{4}_{2}\mathrm{He}$$

Because these reactions involve the capture of positively charged particles, they usually produce a *neutron-poor* nuclide.

Artificial radionuclides are also synthesized in nuclear reactors, which are excellent sources of slow-moving or **thermal neutrons**. The absorption of a neutron usually results in a *neutron-rich* nuclide. The following neutron absorption reaction occurs in the cooling systems of nuclear reactors cooled with liquid sodium metal.

$$^{23}_{11}\mathrm{Na} + ^{1}_{0}n \rightarrow ^{24}_{11}\mathrm{Na} + \gamma$$

In 1940, absorption of thermal neutrons was used to synthesize the first elements with atomic numbers larger than the heaviest naturally occurring element, uranium. The first of these truly artificial elements were neptunium and plutonium, which were synthesized by Edwin M. McMillan and Philip H. Abelson by irradiating ^{238}U with neutrons to form ^{239}U

$$^{238}_{92}\text{U} + {}^{1}_{0}n \rightarrow {}^{239}_{92}\text{U} + \gamma \quad \text{(neutron capture)}$$

which undergoes β-decay to form ^{239}Np and then ^{239}Pu.

$$^{239}_{92}\text{U} \rightarrow {}^{239}_{93}\text{Np} + {}^{0}_{-1}e$$
$$^{239}_{93}\text{Np} \rightarrow {}^{239}_{94}\text{Pu} + {}^{0}_{-1}e$$

Larger bombarding particles were eventually used to produce even heavier transuranium elements.

$$^{253}_{99}\text{Es} + {}^{4}_{2}\text{He} \rightarrow {}^{256}_{101}\text{Md} + {}^{1}_{0}n$$
$$^{246}_{96}\text{Cm} + {}^{12}_{6}\text{C} \rightarrow {}^{254}_{102}\text{No} + 4{}^{1}_{0}n$$

The half-lives for α-decay and spontaneous fission decrease as the atomic number of the element increases. Element 104, for example, has a half-life for spontaneous fission of 0.3 s. Elements, therefore, become harder to characterize as the atomic number increases.

$$^{251}_{98}\text{Cf} + {}^{32}_{16}\text{S} \rightarrow {}^{282}_{114}\text{X} + {}^{1}_{0}n$$

Solved Example 14-30

To what stable isotope from $^{208}_{82}$Pb, $^{209}_{83}$Bi and $^{207}_{82}$Pb would $^{257}_{103}$Lr decay to?

Solution

$^{257}_{103}$Lr belongs to $(4n + 1)$ series, so it decays to $^{209}_{83}$Bi.

Solved Example 14-31

Which out of $^{206}_{82}$Pb, $^{207}_{82}$Pb, $^{208}_{82}$Pb and $^{209}_{83}$Bi is the terminal member of the naturally occurring radioactive series which begins with $^{235}_{92}$U?

Solution

Out of the given list, only $^{207}_{82}$Pb is the member of $(4n + 3)$ series. The emission of α, β or γ particles would change the mass number by 0 or 4, so the daughter nuclei must also be in the same series as the parent nuclei.

14.11 | TRANSMUTATION

Both the energy and the mass of a bombarding particle enter the target nucleus at the moment of capture. The energy of the new nucleus, called a **compound nucleus**, quickly becomes distributed among all of the nucleons, but the nucleus is nevertheless rendered somewhat unstable. To get rid of the excess energy, a compound nucleus generally ejects something (a neutron, proton, or electron) and often emits γ-radiation as well. This leaves a new nucleus of an isotope different than the original target, so a transmutation has occurred overall.

Ernest Rutherford observed the first example of artificial transmutation. He let α-particles pass through a chamber containing nitrogen atoms, an entirely new radiation was generated, one much more penetrating than α-radiation. It proved to be a stream of protons. Rutherford was able to show that the protons came from the decay of the compound nuclei of fluorine-18, produced when nitrogen-14 nuclei captured bombarding α-particles.

$$\underset{\alpha\text{-particle}}{{}^{4}_{2}\text{He}} + \underset{\substack{\text{Nitrogen}\\ \text{nucleus}}}{{}^{14}_{7}\text{N}} \rightarrow \underset{\substack{\text{Fluorine}\\ \text{(compound}\\ \text{nucleus)}}}{{}^{18}_{9}\text{F}^{*}} \rightarrow \underset{\substack{\text{Oxygen (a radioactive}\\ \text{but stable isotope)}}}{{}^{17}_{8}\text{O}} + \underset{\substack{\text{Proton}\\ \text{(high energy)}}}{{}^{1}_{1}\text{H}}$$

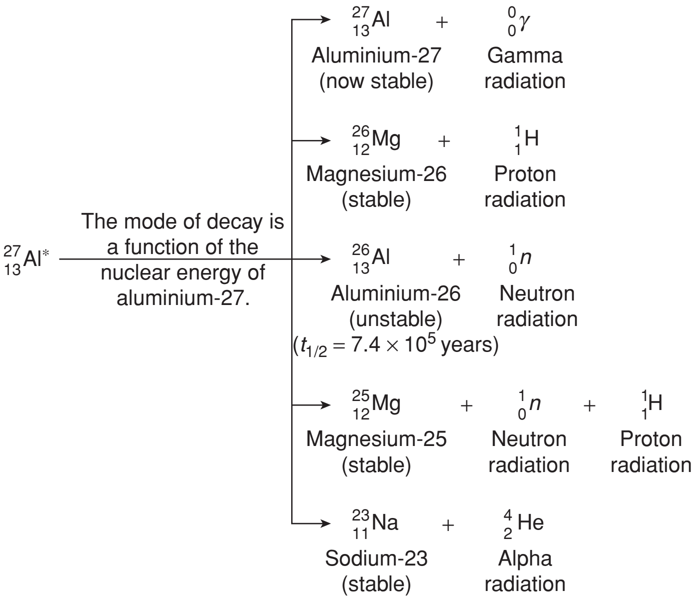
In the synthesis of α-particles from lithium-7, protons are used as bombarding particles. The resulting compound nucleus, that of beryllium-8, splits in two.

$$\underset{\text{Proton}}{{}^{1}_{1}\text{H}} + \underset{\text{Lithium}}{{}^{7}_{3}\text{Li}} \rightarrow \underset{\text{Beryllium}}{{}^{8}_{4}\text{Be}^{*}} \rightarrow \underset{\alpha\text{-particles}}{2\,{}^{4}_{2}\text{He}}$$

A given compound nucleus can be made in a variety of ways. Aluminum-27, for example, forms by any of the following routes.

$$^{4}_{2}\text{He} + ^{23}_{11}\text{Na} \rightarrow ^{27}_{13}\text{Al}^*$$
$$^{1}_{1}\text{H} + ^{26}_{12}\text{Mg} \rightarrow ^{27}_{13}\text{Al}^*$$
$$^{2}_{1}\text{H} + ^{25}_{12}\text{Mg} \rightarrow ^{27}_{13}\text{Al}^*$$

Each path gives the compound nucleus $^{27}_{13}\text{Al}^*$ a different amount of energy. Depending on this energy, different paths of decay are available, and all of the following routes have been observed. They illustrate how the synthesis of such a large number of synthetic isotopes, some stable and others unstable, has been possible.


$^{27}_{13}\text{Al}^*$
The mode of decay is a function of the nuclear energy of aluminium-27.
$^{27}_{13}\text{Al}$ + $^{0}_{0}\gamma$
Aluminium-27 (now stable)
Gamma radiation
$^{26}_{12}\text{Mg}$ + $^{1}_{1}\text{H}$
Magnesium-26 (stable)
Proton radiation
$^{26}_{13}\text{Al}$ + $^{1}_{0}n$
Aluminium-26 (unstable)
Neutron radiation
($t_{1/2} = 7.4 \times 10^5$ years)
$^{25}_{12}\text{Mg}$ + $^{1}_{0}n$ + $^{1}_{1}\text{H}$
Magnesium-25 (stable)
Neutron radiation
Proton radiation
$^{23}_{11}\text{Na}$ + $^{4}_{2}\text{He}$
Sodium-23 (stable)
Alpha radiation

Transmutation for Nuclear Synthesis

Over a thousand isotopes have been made by transmutations; most do not occur naturally. The naturally occurring radioactive isotopes above atomic number 83 all have very long half-lives. Others might have existed, but their half-lives probably were too short to permit them to last into our era. All of the elements beyond neptunium (atomic number 93 and higher, known as the **transuranium elements**) are synthetic. Elements from atomic numbers 93 to 103 complete the actinoid series of the periodic table, which starts with element 90, thorium. Beyond this series, elements 104–116 and 118 have also been made.

To make the heaviest elements, bombarding particles larger than neutrons are used, such as α-particles or the nuclei of heavier atoms. For example, element 110 (darmstadtium, Ds) was made when a neutron was ejected from the compound nucleus formed by the fusion of nickel-62 and lead-208.

$$^{62}_{28}\text{Ni} + ^{208}_{82}\text{Pb} \rightarrow ^{270}_{110}\text{Ds} \rightarrow ^{269}_{110}\text{Ds} + ^{1}_{0}n$$

Similarly, some atoms of element 111 (roentgenium, Rg) formed when a neutron was lost from the compound nucleus made by bombarding bismuth-209 with nickel-64. Most of these heavy atoms are extremely unstable, with half-lives measured in fractions of milliseconds. An exception is element 114; two isotopes have been detected with half-lives reported to be in seconds.

14.12 | NUCLEAR REACTIONS

Nuclear reaction is a process in which two nuclei, or a nucleus of an atom and a subatomic particle such as a proton, neutron, high energy electron or α-particle from outside the atom, react to produce one or more new elementary particles (nuclides). Thus, a nuclear reaction must cause a transformation of at least one elementary particle to another. Nuclear reactions are represented in the same manner as chemical reactions. The rules for balancing a nuclear equation are as follows:

1. The sum of the mass numbers on each side of the arrow must be the same.
2. The sum of the atomic numbers (nuclear charge) on each side of the arrow must be the same.
3. The number of neutrons, protons and atoms of each element are balanced on both sides of the equation.

Nuclear reactions differ from chemical reactions in terms of energy considerations. The energies associated with nuclear reactions are several orders of magnitude larger than those associated with chemical reactions. These reactions may occur naturally, as observed in the Sun and other stars, generating both heat and light energy. These reactions may also be induced artificially by bombarding a nucleus with γ-rays or different particles such as neutrons, positrons, etc. Some important types of nuclear reactions are:

1. **Particle capture reaction:** In these reactions, the particle used for bombarding is absorbed by the substance, with or without the emission of γ-radiation. For example,

$$^{27}_{13}\mathrm{Al} + {}^{1}_{0}n \rightarrow {}^{28}_{13}\mathrm{Al} + \gamma$$

2. **Particle-particle reaction:** In these reactions, the collision of a nucleus with the bombarding particle leads to formation of a new nucleus and a new elementary particle. Most of the nuclear reactions fall in this category. For example,

$$^{14}_{7}\mathrm{N} + {}^{1}_{0}n \rightarrow {}^{14}_{6}\mathrm{C} + {}^{1}_{0}\mathrm{H}$$

3. **Spallation reaction:** In these reactions, high energy projectiles remove a fragment of the heavy nucleus to form two new nuclei and a new elementary particle. For example,

$$^{75}_{33}\mathrm{As} + {}^{2}_{1}\mathrm{H} \rightarrow {}^{56}_{25}\mathrm{Mn} + {}^{1}_{1}\mathrm{H} + 12\,{}^{1}_{0}n$$

4. **Fission reaction:** In these reactions, a heavy nucleus is broken down into two heavy or medium fragments and is accompanied by release of neutrons and large amount of energy. For example,

$$^{235}_{92}\mathrm{U} + {}^{1}_{0}n \rightarrow {}^{139}_{56}\mathrm{Ba} + {}^{94}_{36}\mathrm{Kr} + 3\,{}^{1}_{0}n$$

5. **Fusion reaction:** In these reactions, light nuclei fuse together to form new nuclei that are comparatively heavy and release a large amount of energy. For example,

$$^{7}_{8}\mathrm{Li} + {}^{1}_{1}\mathrm{H} \rightarrow 2\,{}^{2}_{4}\mathrm{He} + \text{Energy}$$

Solved Example 14-32

Calculate the energy released in MeV from the reaction:

$$^{10}_{5}\mathrm{B} + {}^{2}_{1}\mathrm{H} \rightarrow {}^{11}_{5}\mathrm{B} + {}^{1}_{1}\mathrm{H}$$

Given atomic masses $^{10}\mathrm{B}$ = 10.01605 amu; $^{11}\mathrm{B}$ = 11.01286 amu; $^{2}\mathrm{H}$ = 2.01472 amu; $^{1}\mathrm{H}$ = 1.00812 amu.

Solution

Now, Δm = Mass of reactants – Mass of products, so

$$\begin{aligned}\Delta m &= (10.01605 + 2.01472) - (11.01286 + 1.00812)\\ &= 12.03077 - 12.02098\\ &= 0.00979 = 9.79 \times 10^{-3}\ \text{amu}\end{aligned}$$

and energy is

$$\Delta m \times 931\ \text{MeV} = 9.79 \times 10^{-3} \times 931 = 9.11449\ \text{MeV}$$

Solved Example 14-33

Lithium bombarded with protons releases two α-particles and energy:

(a) Write the nuclear reaction.
(b) Calculate the loss in mass.
(c) Calculate the nuclear energy.

Given atomic masses: Li = 7.01601 amu, H = 1.00812 amu and He = 4.00260 amu.

Solution

(a) The nuclear reaction is $^{7}_{8}\mathrm{Li} + {}^{1}_{1}\mathrm{H} \rightarrow 2\,{}^{2}_{4}\mathrm{He} + \text{Energy}$

(b) Loss in mass, Δm = Mass of reactants – Mass of products, thus,

$$\Delta m = (7.01601 + 1.00812) - (2 \times 4.00260)$$
$$= 8.02413 - 8.00520 = 0.01893 \text{ amu}$$

(c) The nuclear energy is given by

$$\Delta mc^2 = \Delta m \times 931 \text{ MeV} = 0.01893 \times 931$$
$$= 17.6238 \text{ MeV}$$

Solved Example 14-34

Nuclear fission of ^{235}U releases energy of the order of 175 MeV per nuclear fission. Calculate the energy released per gram of ^{235}U undergoing fission.

Solution

The number of nuclei present per gram of ^{235}U can be calculated as follows:

235 g of uranium contains 6.023×10^{23} nuclei. Therefore,

$$1\text{g of uranium contains} = \frac{6.023 \times 10^{23}}{235} = 2.56 \times 10^{21} \text{ nuclei}$$

Given that the energy released per nucleus fission = 175 MeV. Therefore, the energy released on fission of the 2.56×10^{21} nuclei present in 1 g of ^{235}U is $175 \times 2.56 \times 10^{21} = 4.48 \times 10^{23}$ MeV.

Nuclear Fission

The graph of binding energy per nucleon in Fig. 14.7 suggests that nuclides with a mass larger than about 130 amu should spontaneously split apart to form lighter, more stable nuclides. Experimentally, we find that spontaneous fission reactions occur for only the very heaviest nuclides—those with mass numbers of 230 or more. Even when they do occur, these reactions are often very slow. The half-life for the spontaneous fission of ^{238}U, for example, is 10^{16} years, or about 2 million times longer than the age of our planet!

We do not have to wait, however, for slow spontaneous fission reactions to occur. By irradiating samples of heavy nuclides with slow-moving thermal neutrons, it is possible to *induce* fission reactions. When ^{235}U absorbs a thermal neutron, for example, it splits into two particles of uneven mass and releases an average of 2.5 neutrons, as shown in Fig. 14.10.

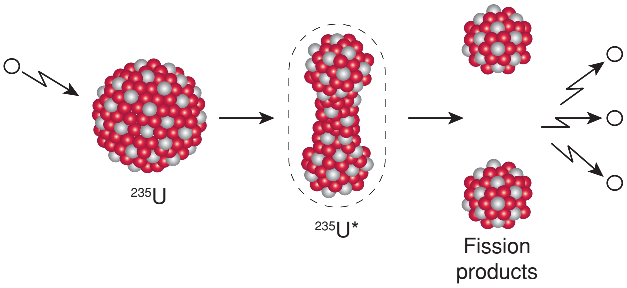


Figure 14.10 The absorption of a neutron by ^{235}U induces oscillations in the nucleus that deform it until it splits into fragments

More than 370 daughter nuclides with atomic masses between 72 and 161 amu are formed in the thermal-neutron-induced fission of ^{235}U, including the two products shown below.

$$^{235}_{92}\text{U} + {}^{1}_{0}n \rightarrow {}^{139}_{56}\text{Ba} + {}^{94}_{36}\text{Kr} + 3^{1}_{0}n$$

Several isotopes of uranium undergo induced fission. But the only naturally occurring isotope in which we can induce fission with thermal neutrons is ^{235}U, which is present at an abundance of only 0.72%. The induced fission of this isotope releases an average of 200 MeV per atom, or 80 million kJ g^{-1} of ^{235}U. The attraction of nuclear fission as a source of power can be understood by comparing this value with the 50 kJ g^{-1} released when natural gas is burned.

Spontaneous fission of ^{238}U or ^{235}U in this reactor produced a very small number of neutrons. But enough uranium was present so that one of these neutrons induced the fission of a ^{235}U nucleus, thereby releasing an average of 2.5 neutrons, which catalyzed the fission of additional ^{235}U nuclei in a chain reaction, as shown in Fig. 14.11. The amount of fissionable material necessary for the chain reaction to sustain itself is called the **critical mass**.

Nuclear Reactors

As we have seen, some of the neutrons released in the chain reaction are absorbed by ^{238}U to form ^{239}U, which undergoes decay by the successive loss of two β^- particles to form ^{239}Pu. ^{238}U is an example of a **fertile nuclide**. It doesn't undergo fission with thermal neutrons, but it can be converted to ^{239}Pu, which does undergo thermal-neutron-induced fission.

Fission reactors can be designed to handle naturally abundant ^{235}U, as well as fuels described as slightly enriched (2–5% ^{235}U), highly enriched (20–30% ^{235}U), or fully enriched (>90% ^{235}U). Heat generated in the reactor core is transferred to a cooling agent in a closed system. The cooling agent is then passed through a series of heat exchangers in which water is heated to steam. The steam produced in these exchangers then drives a turbine that generates electrical power. There are two ways of specifying the power of such a plant: the thermal energy produced by the reactor or the electrical energy generated by the turbines. The electrical capacity of the plant is usually about one-third of the thermal power. It takes 10^{11} fissions per second to produce 1 watt of electrical power. As a result, about 1 g of fuel is consumed per day per megawatt of electrical energy produced

The basic principle and main components of a nuclear power reactor are described as follows. The energy released from fission of fissionable material (e.g., enriched ^{235}U) is harnessed as heat and is used to produce steam, which drives the turbine to produce electricity. The principle is somewhat similar to that of the other electricity generators, the only difference being that nuclear fuels are used here for the purpose. The parts inside the core of a nuclear reactor and their functions are as follows:

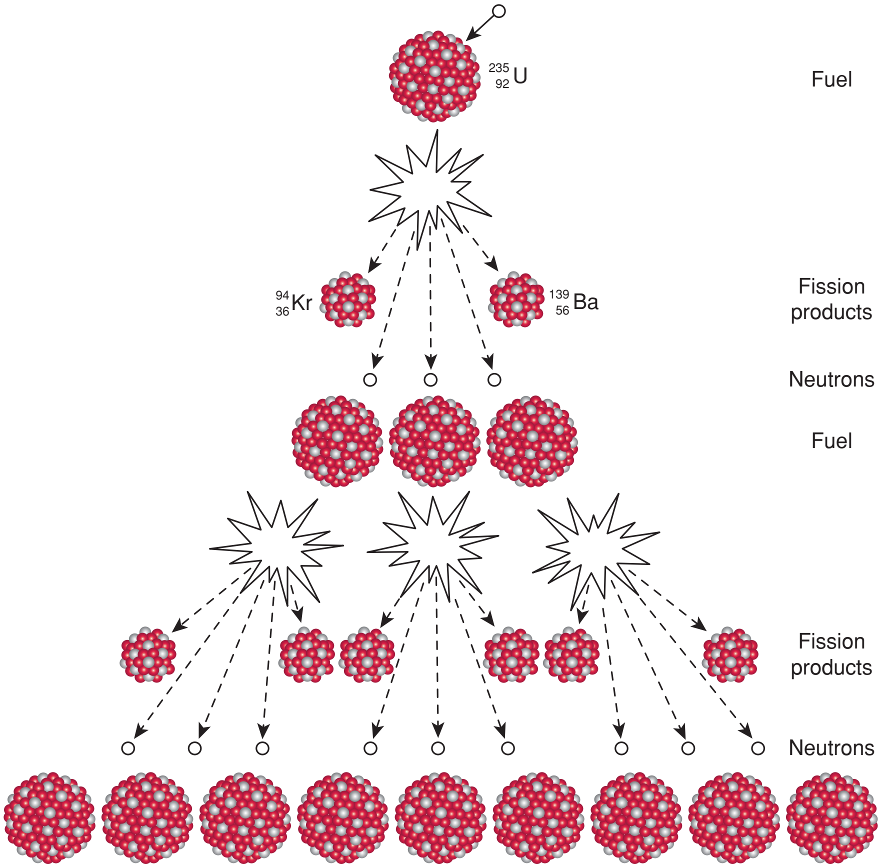


Figure 14.11 Chain reactions occur when the substance needed to start the reaction is regenerated in the course of the reaction.

1. **Fuel rods:** These are made up of hundreds of ^{235}U pellets stacked with each other. These rods are arranged into fuel assemblies inside the core.
2. **Moderator:** Its function is to slow down the neutrons, because only neutrons of a certain speed get captured by the nucleus and hence cause fission. In most cases, water is used as a moderator.
3. **Control rods:** These are made of materials that are highly efficient neutron capturers, for example, cadmium and boron. These rods can be inserted into or withdrawn from the reactor core to control the rate of reaction.
4. **Coolant:** It is used to absorb heat from the reactor. Water is generally used as a coolant.
5. **Steam generator:** It generates steam to spin the turbine (not used in boiling water reactors).
6. **Containment:** It is a shield made of concrete and steel to protect the nuclear reactor from the environment and to protect the environment from any radiation due to malfunction.

The parts outside the reactor core are the turbines, the heat exchanger and part of the cooling system. A boiling water reactor is shown in Fig. 14.12.

Nuclear reactors may also be classified in different ways, depending on the type of coolant, moderator and fuels used. On the basis of neutron energy, they may be of two types:

1. **Thermal neutron reactors:** The nuclear fission in these reactors are controlled by use of moderator and coolant.
2. **Fast neutron reactors:** The nuclear fission in these reactors is carried out by unmoderated fast neutrons. These are generally cooled by liquid metal.

Breeder Reactors

Reactors in which the ratio of the ^{239}Pu or ^{233}U produced to the ^{235}U consumed is greater than 1 generate more fuel than is consumed. Such reactors are known as *breeders*. Thus, breeder reactors generate new fissionable material at a rate greater than their consumption rate. Due to their superior fuel economy, they are highly in demand. Normal reactors consume less than 1% of the natural uranium, while breeder reactors can utilize a much greater amount of initial fissionable material, and can consume almost all the remaining initial material too by reprocessing. While normal reactors use naturally occurring uranium, which has very small quantities of fissile ^{235}U, breeder reactors can be designed to utilize thorium, which is more abundant than uranium.

Breeding ratio is the measure of the efficiency of a reactor. It is the average number of fissile atoms created per fission event. There are two types of breeder reactors:

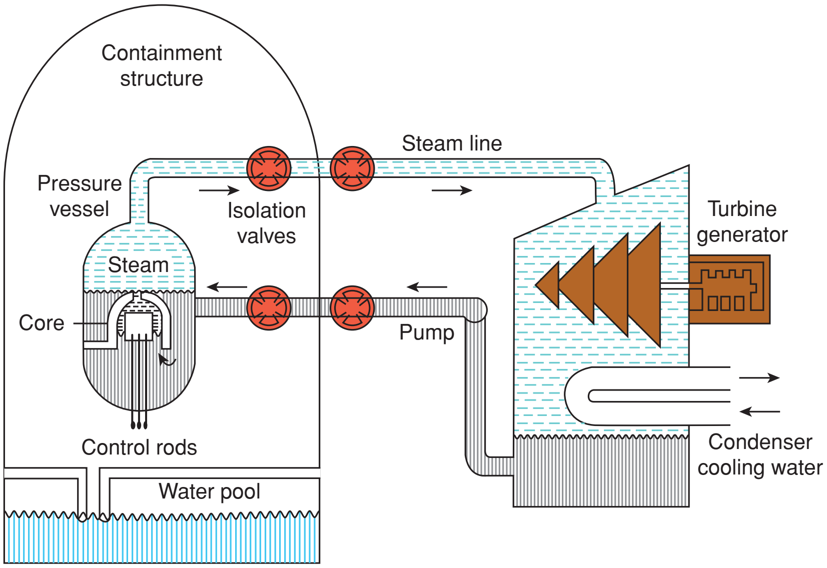


Figure 14.12 A boiling water reactor.

1. **Fast breeder reactor:** This uses plutonium as the initial fuel, and thereafter only natural uranium. Therefore, this fuel cycle is termed as plutonium economy.
2. **Thermal breeder reactor:** This type of reactor uses enriched uranium, or plutonium, or mixed oxide fuel as the initial fuel, and thereafter requires only thorium as the input. ^{232}Th produces ^{233}U after neutron capture and β-decay.

The key to an efficient breeder reactor is a fuel that gives the largest possible number of neutrons released per neutron absorbed. The breeder reactors being built today use a mixture of PuO_2 and UO_2 as the fuel and fast neutrons to activate fission. Fast neutrons carry energy of at least several KeV and therefore travel 10,000 or more times faster than thermal neutrons. ^{239}Pu in the fuel assembly absorbs one of these fast neutrons and undergoes fission with the release of three neutrons. ^{238}U in the fuel then captures one of these neutrons to produce additional ^{239}Pu.

The advantage of breeder reactors is obvious – they mean a limitless supply of fuel for nuclear reactors. There are significant disadvantages, however. Breeder reactors are more expensive to build. They are also useless without a subsidiary industry to collect the fuel, process it, and ship the ^{239}Pu to new reactors.

It is the reprocessing of ^{239}Pu that concerns most of the critics of breeder reactors. ^{239}Pu is so dangerous as a carcinogen that the nuclear industry places a limit on exposure to this material that assumes workers inhale no more than 0.2 μg of plutonium over their lifetimes. There is also concern that the ^{239}Pu produced by these reactors might be stolen and assembled into bombs by terrorist organizations.

Nuclear Fusion

The graph of binding energy per nucleon in Fig. 14.7 suggests another way of obtaining useful energy from nuclear reactions. Fusing two light nuclei can liberate as much energy as the fission of ^{235}U or ^{239}Pu. The fusion of four protons to form a helium nucleus and two positrons, for example, generates 24.7 MeV of energy.

$$4\,{}^{1}_{1}\mathrm{H} \rightarrow {}^{4}_{2}\mathrm{He} + 2\,{}^{0}_{+1}e^{-}$$

Most of the energy radiated from the surface of the sun is produced by the fusion of protons to form helium atoms within its core.

Fusion reactions have been duplicated in man-made devices. The decision was made to develop the weapon, and the first artificial fusion reaction occurred when the hydrogen bomb was tested in November 1952.

The reaction that is most likely to fuel the first fusion reactor is the thermonuclear *d–t*, or deuterium–tritium, reaction. This reaction fuses two isotopes of hydrogen, deuterium (^{2}H) and tritium (^{3}H), to form helium and a neutron.

$${}^{2}_{1}\mathrm{H} + {}^{3}_{1}\mathrm{H} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{1}_{0}n$$

If we consider the implications of this reaction, we can begin to understand why it is called a **thermonuclear reaction** and why it is so difficult to produce helium in a controlled manner. The *d–t* reaction requires that we fuse two positively charged particles. This means that we must provide enough energy to overcome the force of repulsion between these particles before fusion can occur. To produce a self-sustaining reaction, we have to provide the particles with enough thermal energy so that they can fuse when they collide.

Each fusion reaction is characterized by a specific *ignition temperature*, which must be surpassed before the reaction can occur. The *d–t* reaction has an ignition temperature above 10^8 K. In a hydrogen bomb, a fission reaction produced by a small atomic bomb is used to heat the contents to the temperature required to initiate fusion. Obtaining the same result in a controlled reaction is much more challenging.

Any substance at temperatures approaching 10^8 K will exist as a completely ionized gas, or *plasma*. The goals of fusion research at present include the following.

1. To achieve the required temperature to ignite the fusion reaction.
2. To keep the plasma together at this temperature long enough to get useful amounts of energy out of the thermonuclear fusion reactions.
3. To obtain more energy from the thermonuclear reactions than is used to heat the plasma to the ignition temperature.

Nuclear Reactions in the Sun

The pressure inside the core of the Sun is high enough, which pushes the hydrogen atoms close to each other. The two hydrogen atoms combine to yield a bigger atom (helium), with release of a large amount of energy. This process is not a single step process, but takes place in multiple steps, which are:

Step 1: Two protons combine to form a deuterium atom, a positron (or antielectron) and a neutrino:

$${}_1^1\text{H} + {}_1^1\text{H} \rightarrow {}_1^2\text{H} + {}_{+1}^{0}e + \nu$$

Step 2: A proton and deuterium combine to form a ^{3}He atom and a γ-ray (photon):

$${}_1^2\text{H} + {}_1^1\text{H} \rightarrow {}_2^3\text{He} + \gamma$$

Step 3: Two ^{3}He atoms combine together to yield a ^{4}He atom and two protons:

$${}_2^3\text{He} + {}_2^3\text{He} \rightarrow {}_2^4\text{He} + {}_1^1\text{H} + {}_1^1\text{H}$$

The net energy released is 26 MeV. These reactions are responsible for 85% of the Sun's energy. The remaining 15% can be accounted for by the following reactions:

Step 1: ${}_2^3$He and ${}_2^4$He combine to form ${}_4^7$Be and a γ- ray (photon):

$${}_2^3\text{He} + {}_2^4\text{He} \rightarrow {}_4^7\text{Be} + \gamma$$

Step 2: The ${}_4^7$Be captures an electron to yield ^{7}Li and a neutrino:

$${}_4^7\text{Be} + \text{Electron} \rightarrow {}_3^7\text{Li} + \text{Neutrino}$$

Step 3: The ${}_3^7$Li combines with a proton to form two ${}_2^4$He atoms, a positron and a neutrino:

$${}_5^8\text{B} \rightarrow 2{}_2^4\text{He} + \text{Positron} + \text{Neutrino}$$

14.13 | BIOLOGICAL EFFECTS OF RADIATION

To understand the biological effects of radiation, we must first understand the difference between **ionizing radiation** and **non-ionizing radiation**. In general, two things can happen when radiation is absorbed by matter: excitation or ionization. *Excitation* occurs when the radiation excites the motion of the atoms or molecules, or excites an electron from an occupied orbital into an empty, higher-energy orbital. *Ionization* occurs when the radiation carries enough energy to remove an electron from an atom or molecule.

Because living tissue is 70–90% water by weight, the dividing line between radiation that excites electrons and radiation that forms ions is often assumed to be equal to the energy required to remove an electron from a neutral water molecule: 1216 kJ mol^{-1}. Radiation that has less energy can only excite the water molecule. It is, therefore, called *non-ionizing radiation*. Radiation that carries more energy than 1216 kJ mol^{-1} can remove an electron from a water molecule and is, therefore, called *ionizing radiation*.

Table 14.3 contains estimates of the energies of various kinds of radiation. Radio waves, microwaves, infrared radiation and visible light are all forms of non-ionizing radiation. X-rays, γ-rays, and α- and β-particles are forms of ionizing radiation. The dividing line between ionizing and non-ionizing radiation in the electromagnetic spectrum falls in the ultraviolet portion of the spectrum. It is therefore useful to divide the UV spectrum into two categories: UV_A and UV_B. Radiation at the high-energy end of the UV spectrum can be as dangerous as X-rays or γ-rays.

Table 14.3 Energies of ionizing and non-ionizing forms of radiation

Radiation	Typical frequency (s^{-1})	Typical energy (kJ^{-1})	
Particles			
α-Particles		4.1×10^{8}	Ionizing radiation
β-Particles		1.5×10^{7}	
Electromagnetic radiation			
Cosmic rays	6×10^{21}	2.4×10^{9}	
γ-Rays	3×10^{20}	1.2×10^{8}	
X-Rays	3×10^{17}	1.2×10^{5}	
Ultraviolet	3×10^{15}	1200	Non-ionizing radiation
Visible	5×10^{14}	200	
Infrared	3×10^{13}	12	
Microwaves	3×10^{9}	1.2×10^{-3}	
Radio waves	3×10^{7}	1.2×10^{-5}	

When ionizing radiation passes through living tissue, electrons are removed from neutral water molecules to produce H_2O^+ ions. Between three and four water molecules are ionized for every 1.6×10^{-17} J of energy absorbed in the form of ionizing radiation.

$$H_2O \rightarrow H_2O^+ + e^-$$

The H_2O^+ ion should not be confused with the H_3O^+ ion produced when acids dissolve in water. The H_2O^+ ion is an example of a *free radical*, which contains an unpaired valence-shell electron. Free radicals are extremely reactive. The radicals formed when ionizing radiation passes through water are among the strongest oxidizing agents that can exist in aqueous solution. At the molecular level, these oxidizing agents destroy biologically active molecules by either removing electrons or removing hydrogen atoms. This often leads to damage to the membrane, nucleus, chromosomes, or mitochondria of the cell that either inhibits cell division, results in cell death, or produces a malignant cell.

Biological Effects of Ionizing Radiation

It takes a great deal of non-ionizing radiation to reach dangerous levels. We can assume, for example, that absorption of enough radiation to produce an increase of about 6°C in body temperature would be fatal. Since the average 70 kg human is 80% water by weight, we can use the heat capacity of water to calculate that it would take about 1.5 million joules of non-ionizing radiation to kill the average human. If this energy were carried by visible light with a frequency of 5×10^{14} s^{-1}, it would correspond to absorption of about seven moles of photons.

Ionizing radiation is much more dangerous. A dose of only 300 J of X-ray or γ-ray radiation is fatal for the average human, even though this radiation raises the temperature of the body by only 0.001°C. α-particle radiation is even more dangerous; a dose equivalent to only 15 J is fatal for the average human. Whereas it takes 7 mol of photons of visible light to produce a fatal dose of non-ionizing radiation, absorption of only 7×10^{-10} mol of the α-particles emitted by ^{238}U is fatal.

There are three ways of measuring ionizing radiation.

1. Measure the *activity* of the source in units of disintegrations per second or curies, which is the easiest measurement to make.
2. Measure the radiation to which an object is *exposed* in units of roentgens by measuring the amount of ionization produced when this radiation passes through a sample of air.
3. Measure the radiation *absorbed* by the object in units of radiation absorbed doses or "rads." This is the most useful quantity, but it is the hardest to obtain.

One **radiation absorbed dose, or rad**, corresponds to the absorption of 10^{-5} J of energy per gram of body weight. Because this is equivalent to 0.01 J kg^{-1}, one rad produces an increase in body temperature of about $2 \times 10^{-6}\,°\text{C}$. At first glance, the rad may seem to be a negligibly small unit of measurement. The destructive power of the radicals produced when water is ionized is so large, however, that cells are inactivated at a dose of 100 rads, and a dose of 400 to 450 rads is fatal for the average human.

Not all forms of radiation have the same efficiency for damaging biological organisms. The faster energy is lost as the radiation passes through the tissue, the more damage it does. To correct for the differences in **radiation biological effectiveness (RBE)** among various forms of radiation, a second unit of absorbed dose has been defined. The **roentgen equivalent man (rem)** is the absorbed dose in rads times the biological effectiveness of the radiation.

$$\text{rems} = \text{rads} \times \text{RBE} \qquad (14.17)$$

Values for the RBE of different forms of radiation are given in Table 14.4.

Table 14.4 The radiation biological effectiveness of various forms of radiation

Radiation	RBE
X-rays and γ-rays	1
β–particles	1
Thermal (slow-moving) neutrons	3
Fast-moving neutrons or protons	10
α–particles or heavy ions	20

The principal effect of low doses of ionizing radiation is to induce cancers, which may take up to 20 years to develop. Cells that are actively dividing are more sensitive to radiation than cells that aren't. Thus cells in the liver, kidney, muscle, brain, and bone are more resistant to radiation than the cells of bone marrow, the reproductive organs, the epithelium of the intestine, and the skin, which suffer the most damage from radiation. Damage to the bone marrow is the main cause of death at moderately high levels of exposure (200 to 1000 rads). Damage to the gastrointestinal tract is the major cause of death for exposures of the order of 100 to 10,000 rads. Massive damage to the central nervous system is the cause of death from extremely high exposures (over 10,000 rads).

The relation between exposure rate and the distance from the source is

$$\text{Radiation} \propto \frac{1}{d^2} \Rightarrow \frac{I_1}{I_2} = \frac{d_2^2}{d_1^2} \qquad (14.18)$$

where I_1 and I_2 are the exposure rates. This relation is also called **inverse square law**.

Solved Example 14-35

Suppose that a radiologist who is 2.0 m from a small, unshielded source of radiation receives 2.8 units of radiation. To reduce the exposure to 0.28 units of radiation, to what distance from the source should the radiologist move?

Solution

We know that $\frac{I_1}{I_2} = \frac{d_2^2}{d_2^2}$. Thus, substituting given values we get

$$d_2 = d_1\sqrt{\frac{I_1}{I_2}} = 2.0\sqrt{\frac{2.8}{0.28}} = 6.3 \text{ m}$$

Solved Example 14-36

What is the activity, in Ci, of a γ-ray source that emits a single 1.67 MeV γ-ray per disintegration, if the dose received at a distance of 1.0 m from the source is 337 m rad h^{-1}?

Solution

For γ-radiation, $6\,AEn\,d^{-2}$ = dose in m rad h^{-1}

$$d = 1.0 \text{ m} \times \left(\frac{100 \text{ cm}}{1 \text{ m}}\right) \times \left(\frac{1 \text{ in}}{2.54 \text{ cm}}\right) \times \left(\frac{1 \text{ ft}}{12 \text{ in}}\right) = 3.3 \text{ ft}$$

$$337 = 6A \times 1.67 \frac{1}{(3.3)^2} \Rightarrow A = 24 \text{ m Ci} = 0.24 \text{ Ci}$$

Solved Example 14-37

If exposure from a distance of 1.60 m gave a worker a dose of 8.4 rem, how far should the worker move away from the source to reduce the dose to 0.50 rem for the same period?

Solution

This calculation makes use of the inverse square law:

$$\frac{I_1}{I_2} = \frac{d_2^2}{d_2^2}$$

Substituting the given values, we get

$$\frac{8.4 \text{ rem}}{0.50 \text{ rem}} = \frac{d_2^2}{(1.60)^2} \Rightarrow d_2 = 6.6 \text{ m}$$

14.14 | APPLICATIONS OF RADIOACTIVITY

Nuclear energy is an environment-friendly energy resource for power generation. A very small amount of nuclear fuel is sufficient for the production of a large amount of energy in nuclear-powered reactors. The use of this fuel results in diminished dependence on fossil fuels. Nuclear fuels also do not emit gases such as CO_2, SO_2 and NO_2 that are released on burning fossil fuels. Emission of these gases is responsible for many problems arising due to indiscriminate use of fossil fuels, such as global warming, greenhouse effect, acid rain, etc. The water that is discharged from the nuclear reactors is free from radiation and is clean enough to conserve wild and aquatic ecosystems.

Nuclear energy is used to enhance the production/yield of crops. The use of nuclear radiation prevents moulding of seeds, delays ripening of fruits and brings about other such desirable changes. Some techniques such as sterile insect technique are useful in control of agricultural pests.

The important applications of radioactivity are in the field of nuclear medicine and carbon dating**.**

Dating by Radioactive Decay

The earth is constantly bombarded by cosmic rays emitted by the sun. The total energy received in the form of cosmic rays is small—no more than the energy received by the planet from starlight. But the energy of a single cosmic ray is very large, of the order of several billion electron volts (≈200 million kJ mol^{-1}). These highly energetic rays react with atoms in the atmosphere to produce neutrons that then react with nitrogen atoms in the atmosphere to produce ^{14}C.

$$^{14}_{7}\text{N} + ^{1}_{0}n \rightarrow ^{14}_{6}\text{C} + ^{1}_{1}\text{H}$$

The ^{14}C formed in this reaction is a neutron-rich nuclide that decays by electron emission with a half-life of 5730 years.

$$^{14}_{6}\text{C} \rightarrow ^{14}_{7}\text{N} + ^{0}_{-1}e$$

Just after World War II, Willard F. Libby proposed a way to use these reactions to estimate the age of carbon-containing substances. The **^{14}C dating** technique for which Libby received the Nobel Prize was based on the following assumptions.

1. ^{14}C is produced in the atmosphere at a more or less constant rate.
2. Carbon atoms circulate among the atmosphere, the oceans, and living organisms at a rate very much faster than they decay. As a result, there is a constant concentration of ^{14}C in all living things.
3. After death, organisms no longer pick up ^{14}C.
4. Thus, by comparing the activity of a sample with the activity of living tissue, we can estimate how long it has been since the organism died.

The natural abundance of ^{14}C is about 1 part in 10^{12}, and the average activity of living tissue is 15.3 disintegrations per minute per gram of carbon. Samples used for ^{14}C dating can include charcoal, wood, cloth, paper, seashells, limestone, flesh, hair, soil, peat, and bone. Since most iron samples also contain carbon, it is possible to estimate the time since iron was last fired by analyzing for ^{14}C.

Potassium–argon dating, for example, has been used to date samples up to 4.3 billion years old. Naturally occurring potassium contains 0.0118% by weight of the radioactive ^{40}K isotope. This isotope decays to ^{40}Ar with a half-life of 1.3 billion years. The ^{40}Ar produced after a rock crystallizes is trapped in the crystal lattice. It can be released, however, when the rock is melted at temperatures up to 2000°C. By measuring the amount of ^{40}Ar released when the rock is melted and comparing it with the amount of potassium in the sample, the time since the rock crystallized can be determined.

Note: The amount of ^{14}C in the atmosphere has not been constant with time. Because of changes in solar activity and the earth's magnetic field, it has varied by as much as ±5%. More recently, contamination from the burning of fossil fuels and the testing of nuclear weapons has caused significant changes in the amount of radioactive carbon in the atmosphere. Radiocarbon dates are therefore reported in years before the present era (B.P.). By convention, the present era is assumed to begin in 1950, when ^{14}C dating was introduced.

The amount of sample that remains and the age of the sample can be determined using integrated form of first-order reaction. This is explained in the following solved examples.

Note: In examples of dating, the rate constant k is used to represent disintegration constant λ.

Solved Example 14-38

The skin, bone, and clothing of an adult female mummy were dated by radiocarbon analysis. How old is this mummy if the sample exhibited 73.9% of the activity of living tissue?

Solution

Because ^{14}C decays by first-order kinetics, the natural log of the ratio of the ^{14}C in the sample today (N) to the amount that would be present if it were still alive (N_0) is proportional to the rate constant for this decay and the time since death.

$$\ln\left(\frac{N}{N_0}\right) = -kt$$

The rate constant for this reaction can be calculated from the half-life of ^{14}C, which is 5730 years.

$$k = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{5730\,y} = 1.210 \times 10^{-4}\ \text{years}^{-1}$$

If the sample retained 73.9% of the activity of living tissue, the ratio of the activity today (N) to the original activity (N_0) is 0.739. Substituting what we know into the integrated form of the first-order rate law gives the following equation.

$$\ln(0.739) = -(1.210 \times 10^{-4}\ \text{years}^{-1})t$$

Solving this equation for the unknown gives an estimate of the time since death.

$$t = 2.50 \times 10^{3}\ \text{years}$$

Solved Example 14-39

The ^{14}C content of an ancient piece of wood was found to be one-eighth of that in living trees. How many years old is this piece of wood ($t_{1/2} = 5730$ years for ^{14}C)?

Solution

For a first order process,

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{5730} = 1.210 \times 10^{-4}\ \text{years}^{-1}$$

Also, $\ln \frac{[A]_0}{[A]_t} = kt$. Therefore,

$$t = \frac{1}{k} \ln \frac{[A]_0}{[A]_t} = \frac{2.303}{1.21 \times 10^{-4}} \log\left(\frac{8}{1}\right) = 1.72 \times 10^{4}\ \text{years}$$

Solved Example 14-40

A wooden door lintel from an excavated site would be expected to have what ratio of carbon-14 to carbon-12 atoms if the lintel is 9.0×10^{3} years old?

Solution

We have $\ln \frac{r_0}{r_t} = kt$, where r_0 and r_t are the ratio of carbon-14 to carbon-12 atoms at $t = 0$ and time t, respectively.

$$\ln\left(\frac{1.2 \times 10^{-12}}{r_t}\right) = (1.21 \times 10^{-4})(9.0 \times 10^{3})$$

or $$\log\left(\frac{1.2 \times 10^{-12}}{r_t}\right) = \frac{(1.21 \times 10^{-4})(9.0 \times 10^{3})}{2.303} = 0.47286$$

Solving, we get $$r_t = \left(\frac{1.2 \times 10^{-12}}{2.97}\right) = 4.0 \times 10^{-13}$$

Solved Example 14-41

A worker in a laboratory unknowingly became exposed to a sample of radiolabeled sodium iodide made from iodine-131 (β-emitter, $t_{1/2} = 8.07$ days). The mistake was realized 28.0 days after the accidental exposure, at which time the activity of the sample was 25.6×10^{-5} Ci g^{-1}. The safety officer needed to know how active the sample was at the time of the exposure. Calculate that value in curies per gram

Solution

This calculation makes use of the first order rate equation, where knowing $[A]_t$, we need to calculate $[A]_0$

$$\ln \frac{[A]_0}{[A]_t} = kt$$

The rate constant for the first-order process is first determined:

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{8.07} = 8.59 \times 10^{-2}\ \text{days}^{-1}$$

Substituting, values, we get

$$\ln \frac{[A]_0}{(25.6 \times 10^{-5}\ \text{Cig}^{-1})} = (8.59 \times 10^{-2}) \times (28.0)$$

Taking the exponential of both sides of the above equation gives

$$\frac{[A]_0}{(25.6 \times 10^{-5}\ \text{Ci g}^{-1})} = e^{2.41} = 11.1$$

Solving for the value of $[A]_0$, we get $[A]_0 = 2.84 \times 10^{-3}$ Ci g^{-1}

Solved Example 14-42

What percentage of caesium chloride made from caesium-137 ($t_{1/2}$ = 30 years; β emitter) remains after 150 years?

Solution

The chemical product is $BaCl_2$. For a first order reaction,

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{30} = 2.30 \times 10^{-2}\ \text{y}^{-1}$$

Also, $\ln\frac{[\text{A}]_0}{[\text{A}]_t} = kt$ or $[\text{A}]_t = [\text{A}]_0 \exp(-kt)$. Substituting values, we get

$$\frac{[\text{A}]_0}{[\text{A}]_t} = \exp[-(2.30 \times 10^{-2})(150)] = 3.13 \times 10^{-2}$$

So, 3.1% of the original sample remains.

Nuclear Medicine

Ever since the first X-ray images were obtained by Roentgen in 1895, ionizing radiation and radionuclides have played a vital role in medicine. This work has been so fruitful that a separate field known as nuclear medicine has developed. Research in this field focuses on either therapeutic or diagnostic uses of radiation.

There are three standard approaches to fighting cancer: surgery, chemotherapy and radiation. Surgery, by its very nature, is invasive. Chemotherapy and classic approaches to radiation therapy are not selective. Research in recent years has therefore examined new approaches to radiation therapy that specifically attack tumor cells, without damaging normal tissue. The technique known as *boron neutron capture therapy* provides an example of this work.

Naturally occurring boron consists of two stable isotopes: ^{10}B (19.7%) and ^{11}B (80.3%). ^{10}B absorbs thermal neutrons to form ^{11}B in a nuclear excited state. Although ^{11}B in its nuclear ground state is stable, this excited ^{11}B nuclide undergoes fission to produce ^{7}Li and an α-particle.

$$^{10}_{5}\text{B} + {}^{1}_{0}n \rightarrow {}^{7}_{3}\text{Li} + {}^{4}_{2}\text{He}$$

Because the energy of a thermal neutron is only about 0.025 eV, the neutrons that are not absorbed do relatively little damage to the normal tissue. The α-particle emitted in this reaction has energy of 2.79 MeV, however, which makes it an extremely lethal form of radiation. The RBE for α-particle radiation is larger than any other particle in Table 14.4 because this relatively massive particle loses energy very efficiently as it collides with matter. Radiation damage from the α-particle is therefore restricted to the immediate vicinity of the tissue that absorbed the thermal neutron.

SOLVED OBJECTIVE QUESTIONS FROM PREVIOUS YEAR PAPERS

1. The more stable isotope of sodium is ^{23}Na. The atom ^{24}Na can undergo radioactive decay via

(A) β^- emission
(B) α emission
(C) β^+ emission
(D) K-electron capture

(IIT-JEE 2003)

Solution

(A) n/p ratio of ^{24}Na nuclide is 13/11 that is, greater than unity and hence radioactive. To achieve stability, it would tend to adjust its n/p ratio to the proper value of unity. This can be done by breaking a neutron into proton and electron. It would tend to adjust its

$$^{1}_{0}n \rightarrow {}^{1}_{+1}\text{H} + {}^{0}_{-1}e \quad (\text{or } \beta)$$

The proton will stay inside the nucleus whereas electron which cannot exist in the nucleus, will be emitted out as β-ray.

2. A nuclear explosion has taken place leading to increase in concentration ^{14}C in nearby areas. ^{14}C concentration is C_1 in nearby areas and C_2 in areas far away. If the age of the fossil is determined to be t_1 and t_2 at the places, respectively, then

(A) the age of the fossil will increase at the place where explosion has taken place and $t_1 - t_2 = \frac{1}{\lambda}\ln\frac{C_1}{C_2}$

(B) the age of the fossil will decrease at the place where explosion has taken place and $t_1 - t_2 = \frac{1}{\lambda}\ln\frac{C_1}{C_2}$

(C) the age of fossil will be determined to be same.

(D) $\frac{t_1}{t_2} = \frac{C_1}{C_2}$

(IIT-JEE 2006)

Solution

(A) This is in accordance with first order kinetics,

$$k = t\ln\frac{C_1}{C_2} \text{ where } t = t_1 - t_2$$

3. A positron is emitted from $^{23}_{11}Na$. The ratio of the atomic mass and atomic number of the resulting nuclide is

(A) 22/10 (B) 22/11
(C) 23/10 (D) 23/12 **(IIT-JEE 2007)**

Solution

(C) On positron emission from nucleus, proton converts into neutron, therefore, atomic number decreases by one but atomic mass remains constant.

$$^{23}_{11}Na \rightarrow {}^{23}_{10}Ne + {}^{0}_{+1}e\,(\beta^+)$$

4. Statement 1: The plot of atomic number (y-axis) vs. number of neutrons (x-axis) for stable nuclei shows a curvature towards x-axis from the line of 45° slope as the atomic number is increased.

Statement 2: Proton–proton electrostatic repulsions begin to overcome attractive forces involving protons and neutrons in heavier nuclides. **(IIT-JEE 2008)**

(A) Statement 1 is True, Statement 2 is True; Statement 2 is a correct explanation for Assertion (statement 1).
(B) Statement 1 is True, Statement 2 is True; Statement 2 is NOT a correct explanation for Statement 1.
(C) Statement 1 is True, Statement 2 is False.
(D) Statement 1 is False, Statement 2 is True.

Solution

(A) If the curve does not bend towards the x-axis then *proton–proton* repulsion would overcome the attractive forces of proton and neutron, therefore, the curve bends down (Fig. 14.13).

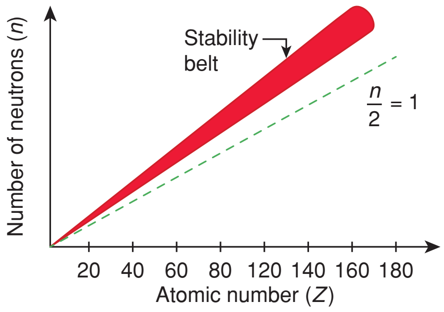


Figure 14.13

5. The total number of α and β particles emitted in the nuclear reaction $^{238}_{92}U \rightarrow {}^{214}_{82}Pb$ is __________. **(IIT-JEE 2009)**

Solution

(8) 6α and 2β particles are emitted which means a total of 8 particles are emitted.

$$^{238}_{92}U \xrightarrow[(=6\,^4_2He)]{-6\alpha} {}^{214}_{80}X \xrightarrow[(2\,^{0}_{-1}e)]{-2\beta} {}^{214}_{82}Pb$$

6. The number of neutrons emitted when $^{235}_{92}U$ undergoes controlled nuclear fission to form $^{142}_{54}Xe$ and $^{90}_{38}Se$ is __________. **(IIT-JEE 2010)**

Solution

(3) $^{235}_{92}U \rightarrow {}^{142}_{54}Xe + {}^{90}_{38}Sr + 3\,^1_0n$ which means that three neutrons are emitted out.

7. Bombardment of aluminium by α–particle leads to its artificial disintegration in two ways, (I) and (II) as shown in Fig. 14.14. Products X, Y and Z, respectively, are,

(A) proton, neutron, positron.
(B) neutron, positron, proton.
(C) proton, positron, neutron.
(D) positron, proton, neutron. **(IIT-JEE 2011)**

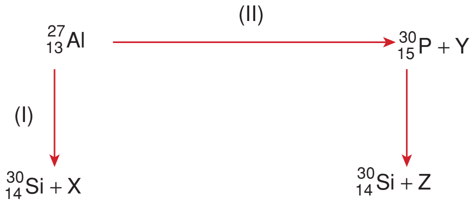


Figure 14.14

Solution

(A) In order to find X, Y, Z we need to equate atomic numbers as well as mass numbers on both the sides.

$$^{27}_{13}Al + {}^{4}_{2}He \rightarrow {}^{30}_{15}P + {}^{1}_{0}n(Y)$$

$$\downarrow \qquad\qquad\qquad \downarrow$$

$$^{30}_{14}Si + {}^{1}_{1}H(X) \qquad {}^{30}_{14}Si_{14} + {}^{0}_{+1}e^-\,(Z)$$

X is a proton ^1_1H, Y is a neutron ^1_0n, Z is a positron $^{0}_{+1}e$.

8. The periodic table consists of 18 groups. An isotope of copper, on bombardment with protons, undergoes a nuclear reaction yielding element X as shown below. To which group, element X belongs in the periodic table?

$$^{63}_{29}Cu + {}^1_1H \rightarrow 6\,^1_0n + \alpha + 2\,^1_1H + X$$ **(IIT-JEE 2012)**

Solution

(8) Considering the reaction (replacing α-particle by ^4_2He)

$$^{63}_{29}Cu + {}^1_1H \rightarrow 6\,^1_0n + {}^4_2He + 2\,^1_1H + X$$

Equating mass numbers on both the sides, we get

$$63 + 1 = 1\times 6 + 4\times 1 + 1\times 2 + X = 64 - 12 = 52$$

Equating atomic numbers on both the sides, we get

$$29 + 1 = 6\times 0 + 2 + 2\times 1 + Y \Rightarrow Y = 30 - 4 = 26$$

So, the element is $^{52}_{26}Fe$ and iron is a d-block element, belonging to Group 8 of the periodic table.

9. In the nuclear transmutation

$${}_{4}^{9}\text{Be} + \text{X} \rightarrow {}_{4}^{8}\text{Be} + \text{Y}$$

(X, Y) is (are)
(A) (γ, n) (B) (p, D) (C) (n, D) (D) (γ, p)

(JEE Advanced 2013)

Solution

(A), (B) The reactions involved are

$${}_{4}^{9}\text{Be} + \gamma \rightarrow {}_{4}^{8}\text{Be} + {}_{0}^{1}n$$

$${}_{4}^{9}\text{Be} + {}_{1}^{1}\text{H} \rightarrow {}_{4}^{8}\text{Be} + {}_{1}^{2}\text{H}$$

10. A closed vessel with rigid walls contains 1 mol of ${}_{92}^{238}\text{U}$ and 1 mol of air at 298 K. Considering complete decay of ${}_{92}^{238}\text{U}$ to ${}_{82}^{206}\text{Pb}$, the ratio of the final pressure to the initial pressure of the system at 298 K is _______.

(JEE Advanced 2015)

Solution

(9) Let us consider that

1 mol of air = X atm

During the reaction of ${}_{92}^{238}\text{U} \rightarrow {}_{82}^{206}\text{Pb}$, 8$\alpha$-particles are released, that is, 8 mol of He particles are released during the reaction. Therefore, 9 mol of gas are present in the vessel.

Thus, total pressure = $X \times 9 = 9$ atm that is, 9 times the original pressure.

11. A photon of hard γ-radiation knocks a proton out of ${}_{12}^{24}\text{Mg}$ nucleus to form

(A) the isotope of parent nucleus.
(B) the isobar of parent nucleus.
(C) the nuclide ${}_{11}^{23}\text{Na}$.
(D) the isobar of ${}_{11}^{23}\text{Na}$.

(AIEEE 2005)

Solution

(C) ${}_{12}^{24}\text{Mg} \rightarrow {}_{11}^{23}\text{Na} + {}_{1}^{1}\text{H}$

12. In the transformation of ${}_{92}^{238}\text{U}$ to ${}_{92}^{234}\text{U}$, if one emission is an α-particle, what should be the other emission(s)?

(A) Two β^- (B) Two β^- and one β^-
(C) One β^- and one γ (D) one β^- and one β^-

(AIEEE 2006)

Solution

(A) ${}_{92}^{238}\text{U} \rightarrow {}_{92}^{238}\text{U} + {}_{2}^{4}\text{He} + 2\,{}_{-1}^{0}e^-$. Change of 4 units in atomic mass is compensated by one α-particle but there should be emission of two β-particles also to compensate atomic number.

13. A radioactive element gets spilled over the floor of a room. Its half-life period is 30 days. If the initial activity is 10 times the permissible value, after how many days will it be safe to enter the room?

(A) 100 days (B) 1000 days
(C) 300 days (D) 10 days

(AIEEE 2007)

Solution

(A) We know that

$$\text{Activity}\left(-\frac{dN}{dt}\right) \propto N$$

or

$$N = N_0\left(\frac{1}{2}\right)^n \Rightarrow \frac{N}{N_0} = \left(\frac{1}{2}\right)^n$$

$$\frac{1}{10} = \left(\frac{1}{2}\right)^n \Rightarrow 10 = 2^n$$

Taking log on both the sides, we get

$$\log = 10 = n \log 2$$

$$n = \frac{1}{0.301} = 3.32 \text{ (as } \log 2 = 0.3010)$$

Therefore, $t = n \times t_{1/2} = 3.32 \times 30 = 99.6$ days.

14. Which of the following nuclear reactions will generate an isotope?

(A) β-particle emission
(B) Neutron particle emission
(C) Positron emission
(D) α-particle emission

(AIEEE 2007)

Solution

(A) Isotopes have same atomic numbers but different mass numbers

$${}_{Z}^{A}\text{X} \rightarrow {}_{Z}^{A-1}\text{X} + {}_{0}^{1}n$$

REVIEW QUESTIONS

1. Give the differences between nuclear fission and nuclear fusion?

2. What do each of the following terms mean: **(a)** thermal neutron, **(b)** nuclear fission, **(c)** fissile isotope and **(d)** nuclear fusion?

3. Pick up the pairs of isotopes and isobars from the following:

$${}_{1}^{1}\text{H},\ {}_{7}^{14}\text{N},\ {}_{8}^{16}\text{O},\ {}_{20}^{40}\text{Ca},\ {}_{8}^{17}\text{O},\ {}_{78}^{198}\text{Pt},\ {}_{18}^{40}\text{Ar},\ {}_{6}^{14}\text{C},\ {}_{78}^{192}\text{Pt}$$

4. What obstacles make constructing a reactor for controlled nuclear fusion especially difficult?

5. Why do fission and fusion reactions produce large quantities of energy?

6. Why would there be a subcritical mass of a fissile isotope? (Why isn't any mass of uranium-235 critical?)

7. ${}_{92}^{234}\text{Th} \rightarrow {}_{2}^{4}\text{He} + 6\,{}_{-1}^{0}e + \text{X}$. Find out atomic number and mass number of the element X. Also identify the element.

8. Why is it easier for a nucleus to capture a neutron than a proton?

9. Complete and balance the following reactions.

(a) ${}_{92}^{235}\text{U} + {}_{0}^{1}n \rightarrow \_\_\_ + {}_{52}^{137}\text{Te} + {}_{40}^{92}\text{Zr}$

(b) ${}_{34}^{86}\text{Se} \rightarrow 2\,{}_{-1}^{0}e + \_\_\_$

10. An α emitter is not used in diagnostic work. Why?

11. What specific property of nuclear radiation is used by the Geiger counter?

12. What does electron capture do to the neutron-to-proton ratio in a nucleus, increase it, decrease it, or leave it alone? Which kinds of radionuclides are more likely to undergo this change, those above or those below the band of stability?

13. Which of the following pairs has longer half-life and why: **(a)** Barium-123 and barium-140, **(b)** tin-112 and indium-112, **(c)** Lanthanum-139 and lanthanum-140?

14. Why should a radionuclide used in diagnostic work have a short half-life? If the half-life is too short, what problem arises?

15. Although lead-164 has two magic numbers, 82 protons and 82 neutrons, this isotope is unknown. Lead-208, however, is known and stable. What problem accounts for the nonexistence of lead-164?

16. How does electron capture generate X-rays?

17. Give the composition of each of the following.

(a) α-particle
(b) β-particle
(c) positron
(d) deuteron

18. Why isn't the sum of the masses of all nucleons in one nucleus equal to the mass of the actual nucleus?

19. Why is the penetrating ability of α-radiation less than that of β- or γ-radiation?

20. Suppose that an atom of argon-37 could decay by either β-emission or electron capture. Which route would it likely take, and why? Write the nuclear equation.

21. Define the terms isotopes, isobars and isotones. Give examples of pairs of nuclides that would be described by each of these terms.

22. Explain why ^{17}Ne, ^{18}Ne and ^{19}Ne decay by positron emission but ^{23}Ne and ^{24}Ne decay by electron emission.

23. Which of the following reactions interconvert isotopes? Which interconvert isobars? Which interconvert isotones?

(a) electron emission
(b) electron capture
(c) positron emission
(d) α emission
(e) neutron emission
(f) neutron absorption
(g) α emission followed by two β^- decays

24. In theory, β-decay could include reactions in which a positron is captured and the charge on the nucleus increases. Explain why the following positron capture reaction does not occur under "normal" conditions.

$${}^{14}_{6}\text{C} + {}^{0}_{+1}e \rightarrow {}^{14}_{7}\text{N} + h\nu$$

25. Calculate the number of electrons, protons and neutrons in both a $^{40}\text{K}^+$ and an $^{127}\text{I}^-$ ion.

NUMERICAL PROBLEMS

1. The amount of ^{14}C isotopes in a piece of wood is found to be one-sixth of its amount present in a fresh piece of wood. Calculate the age of wood. Half-life of ^{14}C is 5577 years.

2. The observed mass of ${}^{56}_{26}$Fe is 55.9375 amu. Using the masses of proton and neutron as 1.00732 amu and 1.00866 amu, respectively, calculate the binding energy per nucleon in MeV and in J.

3. The binding energy per nucleon for ^{12}C is 7.68 MeV and that for ^{13}C is 7.47 MeV. Calculate the energy required to remove a neutron from ^{13}C.

4. The observed mass of ${}^{16}_{8}$O atom is 15.99491 amu. Calculate the average binding energy in MeV per nuclear particle in this isotope.

5. The activity of the ^{14}C in living tissue is 15.3 disintegrations per minute per gram of carbon. The limit for reliable determination of ^{14}C ages is 0.10 disintegration per minute per gram of carbon. Calculate the maximum age of a sample that can be dated accurately by radiocarbon dating if the half-life for the decay of ^{14}C is 5730 years.

6. Measurements on the linen wrappings from the scrolls suggest that the scrolls contain about 79.5% of the ^{14}C expected in living tissue. How old are these scrolls? (^{14}C: $t_{1/2} = 5730$ yr)

7. Calculate the number of disintegrations per minute in a 1.00 mg sample of ^{238}U, assuming that the half-life is 4.47×10^9 years.

8. Calculate the half-life for the decay of ^{39}Cl if a 1.000 g sample decays to 0.125 g in 165 min.

9. Calculate the number of neutrons in the atom produced after the emission of an α-particle in ${}^{238}_{92}$X atom.

10. The half-life of a radioactive isotope is 47.2 s. Calculate N/N_0 left after one hour.

11. Calculate the energy in kilojoules per mole for an X-ray that has a frequency of 3×10^{17} s^{-1}. How do the results of this calculation compare with the energy required to remove an electron from water?

12. 3.125×10^{-8} γ-atoms of radon exists in equilibrium with 1 g of radium at 0°C and 1 atm pressure. The disintegration constant of Ra is 1.48×10^{-11} s^{-1}. Calculate the disintegration constant of radon.

13. Radium-226 undergoes α-ray change, its half-life is 1620 years. What is the activity (rate of disintegration) of 0.001 g of the sample?

14. Suppose that a radiologist who is 2.0 m from a small, unshielded source of radiation receives 2.8 units of radiation. To reduce the exposure to 0.28 units of radiation, to what distance from the source should the radiologist move?

15. One gram of ${}^{198}_{79}$Au ($t_{1/2} = 65$ h) decays by β-emission to produce stable mercury.

(a) Write the nuclear reaction for the process.
(b) How much mercury will be present after 260 h?

16. ^{14}C is believed to be formed in the upper atmosphere by an (n, p) process on ^{14}N. What is Δm for this reaction?

($^{14}N = 14.00307$ amu, $^{14}C = 14.00324$ amu, $^{1}H = 1.00783$ amu and $^{1}n = 1.008665$ amu)

17. Natural magnesium consists of ^{24}Mg, ^{25}Mg and ^{26}Mg. Calculate the average atomic weight of natural magnesium, if the content of the individual isotopes in atomic % is 78.6, 10.1 and 11.3, respectively.

18. A freshly cut piece of wood gives 16100 counts of β-ray emission per minute per kg and an old wooden bowl gives 13200 counts per minute per kg. Calculate the age of the wooden bowl. The half-life period of ^{14}C is 5568 years.

19. Uranium ($^{235}_{92}Fe$) decays with emission of α- and β-particles to form ultimately lead $^{207}_{82}Pb$. How many α- and β-particles are emitted per atom of lead produced?

20. A carbon sample from the frame of a picture gives 7 counts of ^{14}C per minute per gram of carbon. If freshly cut wood gives 15.3 counts of ^{14}C per minute, calculate the age of the frame ($t_{1/2} = 5570$ years).

21. Calculate the activity in curies for 1.00 mg samples of the following isotopes of uranium.

(a) ^{228}U, $t_{1/2} = 9.3$ min, **(b)** ^{230}U, $t_{1/2} = 20.8$ days
(c) ^{236}U, $t_{1/2} = 2.39 \times 10^{7}$ years

22. The half-life time for decomposition of Ra is 1590 years. Calculate the rate constant in s^{-1}. In how many years will three quarters of a given amount of Ra disappear?

23. $^{234}_{90}Th$ disintegrates to $^{206}_{82}Pb$ as the final product. How many α- and β-particles are emitted during this process?

24. The half-life of ^{14}C is 5730 years.

(a) What fraction of the original ^{14}C would a sample of $CaCO_3$ have after 11460 years?

(b) What fraction of the original ^{14}C would still remain after 13000 years?

25. One gram of a radioactive isotope of sodium decays to 0.25 g in one day and six hours. How much time will it take for the radioactivity to fall to l/10th of its original value?

26. Calculate the binding energy of ^{6}Li in MeV per atom if the exact mass of this nuclide is 6.01512 amu. Calculate the binding energy per nucleon.

27. A neutron breaks into a proton and an electron. Calculate the energy produced in this reaction in MeV. Mass of electron, proton and neutron are 9×10^{-31} kg, 1.6725×10^{-27} kg and 1.6747×10^{-27} kg, respectively.

28. Uranium-238 (atomic number 92) during a series of disintegration loses 8α- and 6β-particles. What will be the atomic mass and atomic number of the new product?

29. Calculate the amount of mass in nanograms that is changed into energy when one mole of liquid water forms by the combustion of hydrogen, all measurements being made at 1 atm and 25 °C. What percentage is this of the total mass of the reactants?

30. The half-life of $^{35}_{17}Cl$ for β-emission is 37.5 min. Given 1.00 g sample at time zero, how long will it be before the sample is reduced to 0.25 g?

31. A sample of technetium-99*m* with a mass of 9.00 ng will have decayed to how much of this radionuclide after 4 half-life periods (about 1 day)?

32. Calculate the binding energy in joules per nucleon of the deuterium nucleus, whose mass is 2.0135 u.

33. During work with a radioactive source, a worker was told that he would receive 50 mrem at a distance of 4.0 m during 30 min of work. What would be the received dose if the worker moved closer, to 0.50 m, for the same period?

34. Smoke detectors contain a small amount of americium-241, which has a half-life of 1.70×10^{5} days. If the detector contains 0.20 mg of ^{241}Am, what is the activity, in becquerels? In microcuries?

35. ^{15}O decays by positron emission with a half-life of 124 s.

(a) Give the proper symbol of the product of the decay.

(b) How much of a 750 mg sample of ^{15}O remains after 5.0 min of decay

36. Iodine-131 is used to treat a disease of the thyroid gland. The amount of ^{131}I used depends on the size of the gland. If the dose is 86 microcuries per gram of thyroid gland, how many grams of ^{131}I should be administered to a patient with a thyroid gland weighing 20 g? Assume all the iodine administered accumulates in the thyroid gland.

37. $^{239}_{94}Pu$ is an α-emitter with a half-life of 24,400 years. Given 1 g sample of this plutonium, how many α-particles will it emit per second?

38. Consider $^{224}Ra \xrightarrow{-\alpha} {}^{220}Rn \xrightarrow{-\alpha} {}^{216}Po$ where $t_{1/2}$ (Ra) = 3.64 years, $t_{1/2}$ (Rn) = 55 s. Determine the N_{Ra}/N_{Rn} ratio once secular equilibrium in which $t_{1/2}$ (parent) $\gg$ $t_{1/2}$ (daughter) or λ (parent) $\ll$ λ (daughter) has been established.

ADDITIONAL OBJECTIVE QUESTIONS

Single Correct Choice Type

1. The radioactivity due to ^{14}C-isotope ($t_{1/2} = 6000$ years) of a sample of wood from an ancient tomb was found to be nearly half that of fresh wood. The tomb is, therefore, about

(A) 3000 years old. (B) 6000 years old.
(C) 9000 years old. (D) 12000 years old.

2. The nucleus resulting from $^{238}_{92}U$ after successive emission of two α- and four β-particles is

(A) $^{230}_{90}Th$ (B) $^{230}_{94}Pu$
(C) $^{230}_{88}Ra$ (D) $^{230}_{92}U$

3. If 8.0 g of radioactive isotope has a half-life of 10 h, the half-life of 2.0 g of the same substance is

(A) 2.5 h (B) 5 h
(C) 10 h (D) 40 h

4. The number of α- and β-particles emitted in the nuclear reaction $^{230}_{90}\text{Th} \rightarrow {}^{212}_{83}\text{Bi}$ are:

(A) 4α and 1β
(B) 3α and 7β
(C) 8α and 1β
(D) 4α and 7β

5. When the difference between mass number and atomic number of atoms of two or more elements are same. The atoms are known as

(A) isotopes.
(B) isobars.
(C) isotones.
(D) nuclear isomers.

6. The nuclei, which are not identical but have the same number of nucleons, represent

(A) isotopes.
(B) isobars.
(C) isotones.
(D) none of these.

7. Which isotope of carbon is most likely to decay by positron emission?

(A) ^{11}C
(B) ^{12}C
(C) ^{13}C
(D) ^{14}C

8. A nuclide of an alkaline earth metal undergoes radioactive decay by emission of the α-particles in succession. The group of the periodic table to which the resulting daughter element would belong to is

(A) Group 4.
(B) Group 6.
(C) Group 14.
(D) Group 16.

9. The radioisotope tritium ($^{3}_{1}\text{H}$) has a half-life of 12.3 years. If the initial amount of tritium is 32 mg, how many milligrams of it would remain after 49.2 years?

(A) 2 mg
(B) 4 mg
(C) 8 mg
(D) 1 mg

10. The half-life period of a radioactive element is 140 days. After 560 days, one gram of the element will reduce to

(A) 0.5 g
(B) 0.25 g
(C) 0.125 g
(D) 0.0625 g

11. β-particle is emitted in radioactivity

(A) by conversion of proton to neutron.
(B) from outermost orbit.
(C) by conversion of neutron to proton.
(D) β-particle is not emitted.

12. The number of neutrons accompanying the formation of $^{139}_{54}\text{Xe}$ and $^{94}_{38}\text{Sr}$ from the absorption of a slow neutron by $^{235}_{92}\text{U}$ followed by nuclear fission is

(A) 0
(B) 2
(C) 1
(D) 3

13. $^{13}_{7}\text{N}$ changes to $^{13}_{6}\text{C}$ by emission of

(A) electron.
(B) neutron.
(C) positron.
(D) proton.

14. Loss of a β-particle is equivalent to

(A) increase of one proton only.
(B) decrease of one neutron only.
(C) both A and B.
(D) none of these.

15. The triad of nuclei that is isotonic is

(A) $^{14}_{6}\text{C}$, $^{15}_{7}\text{N}$, $^{17}_{9}\text{F}$
(B) $^{12}_{6}\text{C}$, $^{14}_{7}\text{N}$, $^{19}_{9}\text{F}$
(C) $^{14}_{6}\text{C}$, $^{14}_{7}\text{N}$, $^{17}_{9}\text{F}$
(D) $^{14}_{6}\text{C}$, $^{14}_{7}\text{N}$, $^{19}_{9}\text{F}$

16. Which of the following nuclides are most likely to be neutron-poor?

(A) ^{3}H
(B) ^{11}C
(C) ^{14}N
(D) ^{40}K

17. An element of atomic weight Z consists of two isotopes of mass number $Z - 1$ and $Z + 2$. Percentage of abundance of the heavier isotope is

(A) 25%
(B) 33.33%
(C) 66.66%
(D) 75%

18. A radioactive sample has a half-life of 1500 years. A sealed tube containing 1 g of the sample will contain after 3000 years

(A) 1 g of the sample
(B) 0.5 g of the sample
(C) 0.25 g of the sample
(D) 0.00 g of the sample

19. If $^{235}_{92}\text{U}$ is assumed to decay only by emitting α- and β-particles. The possible product of decay is

(A) $^{231}_{89}\text{Ac}$
(B) $^{225}_{89}\text{Ac}$
(C) $^{230}_{89}\text{Ac}$
(D) $^{227}_{89}\text{Ac}$

20. The number of neutrons in the parent nucleus which give $^{14}_{7}\text{N}$ on β-emission is

(A) 6
(B) 7
(C) 8
(D) 14

21. After the emission of an α-particle from the atom $^{238}_{92}\text{X}$, the number of neutrons in the atom will be

(A) 138
(B) 140
(C) 144
(D) 150

22. Gamma rays are

(A) high energy electrons.
(B) low energy electrons.
(C) high energy electromagnetic waves.
(D) high energy positrons.

23. $^{27}_{13}\text{Al}$ is a stable isotope. $^{29}_{13}\text{Al}$ is expected to disintegrate by

(A) α-emission.
(B) β-emission.
(C) positron emission.
(D) proton emission.

24. Loss of α-particle is equivalent to

(A) loss of two neutrons only.
(B) loss of two protons only.
(C) loss of two neutrons and loss of two protons.
(D) none of these.

25. If half-life of a substance is 5 years, then the total amount of substance left after 15 years when initial amount is 64 g is

(A) 16 g
(B) 2 g
(C) 32 g
(D) 8 g

26. If m_0 is the initial mass of the nuclei, the mass of undecayed radioactive isotope at the end of the nth half-life is

(A) $2^{n} m_0$
(B) $2^{-n} m_0$
(C) $n^{-2} m_0$
(D) $n^{2} m_0$

27. $^{238}_{92}\text{U}$ emits 8α-particles and 6β-particles. The n/p ratio in the product nucleus is

(A) 60/41
(B) 61/40
(C) 62/41
(D) 61/42

28. Number of α-particles emitted per second by a radioactive element falls to 1/16 of its original value in 48 days. The half-life of the emitter is
(A) 48 days
(B) 16 days
(C) 12 days
(D) 8 days

29. Radioactive disintegration differs from a chemical change in
(A) an exothermic change.
(B) a spontaneous process.
(C) a nuclear process.
(D) a unimolecular first order reaction.

30. Which of the following does not characterize X-rays?
(A) The radiation can ionize gases.
(B) It causes ZnS to fluoresce.
(C) Deflected by electric and magnetic fields.
(D) It has wavelengths shorter than ultraviolet rays.

31. Neutrons can disintegrate to give
(A) a proton and an electron.
(B) a positron and an electron.
(C) a proton and a positron.
(D) a proton and γ-radiations.

32. In a certain radioactive decay, an electron is emitted. It comes out from
(A) outermost orbit of the atom.
(B) inner shells of the atom.
(C) nucleus of the atom.
(D) none of these.

33. Which of the following nuclei is unstable?
(A) ${}^{10}_{5}B$
(B) ${}^{10}_{4}Be$
(C) ${}^{14}_{7}N$
(D) ${}^{16}_{8}O$

34. When passing through a magnetic field, the greatest deflection is experienced by
(A) α-rays.
(B) β-rays.
(C) γ-rays.
(D) all show equal deflection.

35. The radiations from a naturally occurring radioactive substance, as seen after deflection by a magnetic field are
(A) definitely α-rays.
(B) definitely β-rays.
(C) both α- and β-rays.
(D) either α- or β-rays.

36. If 3/4 quantity of a radioactive element disintegrates in 2 h, its half-life would be
(A) 1 h.
(B) 45 min.
(C) 30 min.
(D) 15 min.

37. In the reaction ${}^{1}_{1}H + {}^{3}_{1}H \rightarrow {}^{4}_{2}He + {}^{0}_{1}n$, if the binding energies of ${}^{1}_{1}H$, ${}^{3}_{1}H$ and ${}^{4}_{2}He$ are a, b and c (MeV), respectively, then energy in MeV released in this reaction is
(A) $a + b + c$
(B) $a + b - c$
(C) $c + a - b$
(D) $\mathrm{c} - a - b$

38. The uranium (mass number 238 and atomic number 92) emits an α-particle, the product has the mass number and atomic number
(A) 236 and 92
(B) 234 and 90
(C) 238 and 90
(D) 236 and 90

39. The end product formed by the disintegration of ${}^{226}_{88}Ra$ is
(A) ${}^{204}_{81}Tl$
(B) ${}^{206}_{82}Pb$
(C) ${}^{222}_{86}Ra$
(D) ${}^{207}_{83}Bi$

40. In the following reaction ${}^{6}_{3}Li + ? \rightarrow {}^{4}_{2}He + {}^{3}_{1}H$, the missing particle is
(A) electron.
(B) neutron.
(C) proton.
(D) deuteron.

41. Nuclides having the same atomic numbers are known as
(A) isomers.
(B) isotopes.
(C) isotones.
(D) isobars.

42. The largest stable nuclei is
(A) ${}^{238}U$
(B) ${}^{235}U$
(C) ${}^{206}Pb$
(D) ${}^{209}Bi$

43. Which one of the following particles is used to bombard ${}^{27}_{13}Al$ to give ${}^{31}_{15}P$ and a neutron?
(A) Proton
(B) Neutron
(C) α-particle
(D) Deuteron

Multiple Correct Choice Type

1. The correct starting material and end product of different disintegration series are:
(A) ${}^{232}U$, ${}^{208}Pb$
(B) ${}^{235}U$, ${}^{206}Pb$
(C) ${}^{237}Np$, ${}^{209}Bi$
(D) ${}^{238}U$, ${}^{207}Pb$

2. Which of the following nuclides are most likely to be neutron-rich?
(A) ${}^{14}C$
(B) ${}^{24}Na$
(C) ${}^{25}Si$
(D) ${}^{27}Al$

3. Which of the following are isotopes?
(A) $20p + 15n$
(B) $20p + 17n$
(C) $20p + 20n$
(D) $18p + 22n$

4. Which of the following statement(s) about radioactivity is (are) correct?
(A) It is a nuclear property.
(B) It does not involve any rearrangement of electrons.
(C) It is not affected by the presence of other elements.
(D) Its rate is affected by change in temperature and/or pressure.

5. Pick up the correct statement(s).
(A) Deuterons are poor bombarding particles than neutrons.
(B) Hydrogen bomb involves only nuclear fusion.
(C) ${}^{239}Pu$ is obtained from ${}^{238}U$ in breeder reactor.
(D) Induced radioactivity and artificial radioactivity are different.

6. A radioactive element X has an atomic number of 100. If decays directly into an element Y which decays directly into an element Z. In both processes, a charged particle is emitted. Which of the following statement(s) would be true?
(A) Y has an atomic number of 101.
(B) Y has an atomic number of 102.
(C) Z has an atomic number of 99.
(D) Z has an atomic number of 100.

7. Decrease in atomic number is observed during
(A) α-emission.
(B) β-emission.
(C) positron emission.
(D) electron capture.

8. Which of the following statement is/are false?
(A) The most radioactive element present in pitchblende is uranium.
(B) Emission of γ-rays changes the mass number but no atomic number.
(C) ^{32}P is used for the treatment of leukemia.
(D) CO_2 present in air contains ^{12}C only.

9. Which isotope of carbon is most likely to decay by electron emission?
(A) ^{11}C (B) ^{12}C
(C) ^{13}C (D) ^{14}C

10. Many elements have non-integral atomic masses because:
(A) they have isotopes.
(B) their isotopes have non-integral masses.
(C) their isotopes have different masses.
(D) the constituents, neutrons, protons and electrons combine to give fractional masses.

11. In the reaction $^{235}_{92}U \rightarrow {}^{231}_{90}Th + {}^{4}_{2}He$, the shortage of two electrons in thorium is due to
(A) conversion of electron to positron.
(B) combination with positron to evolve energy.
(C) annihilation.
(D) absorption in the nucleus.

12. Which of the following are isobars?
(A) $20p + 17n$ (B) $18p + 22n$
(C) $20p + 20n$ (D) $20p + 15n$

13. Nuclear reactions accompanied with emission of neutron(s) are
(A) $^{27}_{13}Al + {}^{4}_{2}He \rightarrow {}^{30}_{15}P$
(B) $^{12}_{6}C \rightarrow {}^{1}_{1}H + {}^{13}_{7}N$
(C) $^{30}_{15}P \rightarrow {}^{30}_{14}Si + {}^{0}_{-1}e$
(D) $^{241}_{96}Am + {}^{4}_{2}He \rightarrow {}^{244}_{97}Bk + {}^{0}_{-1}e$

14. Which of the following is (are) false?
(A) Loss of β-particle produces an isobar.
(B) Loss of one a two β-particles produces an isotope.
(C) Loss of mass takes place only during nuclear fusion or fission.
(D) Uranium is a transuranic element.

15. A radioactive element is present in Group 8 of the periodic table. If it emits one α-particle, the new position of the nuclide will be
(A) Group 6 (B) Group 12
(C) Group 8 (D) Group 11

16. Which of the following does do not consist of particles of matter?
(A) α-rays (B) β-rays
(C) γ-rays (D) X-rays

17. Isotone(s) of $^{76}_{32}Ge$ is (are)
(A) $^{77}_{32}Ge$ (B) $^{77}_{33}As$
(C) $^{77}_{34}Se$ (D) $^{78}_{34}Se$

18. The moderator used in atomic pile is
(A) heavy water. (B) cadmium.
(C) uranium. (D) graphite.

Assertion–Reasoning Type

Choose the correct option from the following:

(A) Statement 1 is True, Statement 2 is True; Statement 2 is the correct explanation for Statement 1.
(B) Statement 1 is True, Statement 2 is True; Statement 2 is NOT the correct explanation for Statement 1.
(C) Statement 1 is True, Statement 2 is False.
(D) Statement 1 is False, Statement 2 is True.

1. Statement 1: Nuclide $^{30}_{13}Al$ is less than $^{40}_{20}Ca$.

Statement 2: Nuclides having odd number of protons and neutrons are generally stable.

2. Statement 1: In a given electric field, β-particles are deflected more than α-particles having larger charge.

Statement 2: β-particles have smaller mass than α-particles.

3. Statement 1: ^{14}C undergoes β-decay.

Statement 2: It has more number of neutrons than those required for stability.

4. Statement 1: ^{235}U undergoes α-decay.

Statement 2: α-decay is observed in all radioactive isotopes with $Z > 82$.

Comprehension Type

Read the paragraphs and answer the questions that follow.

Paragraph I

Natural radioactivity process continues till stable nuclei are formed. All the nuclei starting from the initial form to the final stable form constitute a series called disintegration series, in which only α-particles and β-particles are eliminated. There are four disintegration series called $4n$, $4n+1$, $4n+2$ and $4n+3$ series. The final product of each series has stable nuclei.

1. The mass of two consecutive members of a series have a difference of how many units?
(A) 1 (B) 2
(C) 3 (D) 4

2. $^{238}_{92}U \rightarrow {}^{206}_{82}Pb$ involves loss of
(A) 8α and 6β particles. (B) 8α and 5β particles.
(C) 8α and 10β particles. (D) 8α and 8β particles.

3. $^{227}_{89}Ac \rightarrow {}^{207}_{82}Pb$ involves loss of
(A) 10 electrons. (B) 8 electrons.
(C) 7 electrons. (D) 4 electrons.

4. The end product of the artificial series is
(A) $^{208}_{82}Pb$ (B) $^{206}_{82}Pb$
(C) $^{209}_{83}Bi$ (D) $^{207}_{82}Pb$

5. Radium-226 belongs to which disintegration series?
(A) $4n$ (B) $4n + 1$
(C) $4n + 2$ (D) $4n + 3$

Paragraph II

Uranium dating technique can be used to predict the age of the earth. The principle behind this technique is that ^{238}U undergoes radioactive decay to form stable ^{206}Pb. The age of the earth can be determined by measuring the ratio of ^{206}Pb to ^{238}U.

$$\frac{\text{Number of atoms of Pb}^{206}\text{ formed}}{\text{Number of atoms of U}^{23}\text{ left}} = e^{-\lambda t-1}$$

Similarly, ^{235}U decays to ^{207}Pb, and ^{232}Th decays to ^{208}Pb. The radioactive isotope of carbon, ^{14}C, produced by the bombardment of nitrogen atoms by neutrons is also used for determining the age of earth by knowing the ratio of $^{14}C/^{12}C$.

6. Which of the following ratio cannot be used for determining the age of a rock?

(A) $^{206}Pb/^{238}U$ (B) $^{206}Pb/^{235}U$

(C) $^{208}Pb/^{232}U$ (D) $^{207}Pb/^{235}U$

7. The ^{14}C atoms are oxidized to carbon dioxide which is reduced to carbohydrate in presence of chlorophyll according to the following general reaction.

$$6CO_2 + 6H_2O \xrightleftharpoons[\text{Chlorophyll}]{h\nu} \text{Carbohydrate} + O_2$$

The oxygen released is coming from

(A) $^{14}CO_2$ (B) H_2O

(C) both A and B (D) $^{12}CO_2$

8. The carbohydrate formed due to reaction involved in the above question has

(A) ^{12}C. (B) ^{14}C.

(C) both A and B. (D) ^{13}C.

9. A sample of ^{238}U (half-life = 4.5×10^9 years) ore is found to contain 23.8 g of ^{238}U and 20.6 g ^{206}Pb. The age of the ore will be

(A) 4.5×10^8 years. (B) 4.49×10^9 years.

(C) 4.4×10^7 years. (D) 7.8×10^8 years.

10. An ore of $^{238}_{92}U$ is found to contain $^{238}_{92}U$ and $^{206}_{82}Pb$ in the weight ratio of 1 : 0.1. If the half-life period of $^{238}_{92}U$ is 4.5×10^9 years, what should be the age of the ore?

(A) 7.097×10^8 years. (B) 7.09×10^6 years.

(C) 4.5×10^8 years. (D) 4.7×10^7 years.

Paragraph III

When a radioactive element is disintegrated, α- and β-particles are evolved from the nucleus. When an α-particle is evolved, the resulting element has an atomic weight less by four units and atomic number less by two units; while in a β-particle evolution, the resulting element has same atomic weight but its atomic number is increased by one.

11. Which of the following combinations of emissions give finally an isotope of the parent element?

(A) α, α, β (B) α, β, β

(C) α, γ, α (D) β, γ, α

12. α-Decay results in

(A) isotope. (B) isobar.

(C) isodiaphere. (D) isotone.

13. How many α and β particles should be emitted from a radioactive nuclide so that an isobar is formed?

(A) $1\alpha, 1\beta$ (B) $2\alpha, 2\beta$

(C) $1\alpha, 2\beta$ (D) $n\beta$

14. A radioactive element belongs to Group 3, it emits one α- and one β-particle to form a daughter nuclide. The position of daughter nuclide will be in

(A) Group 2. (B) Group 1.

(C) Group 12. (D) Group 4.

Integer Answer Type

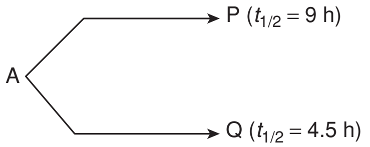
The answer is a **non-negative integer**.

1. The element $^{A}_{Z}M$ undergoes one α-emission and __________ successive β emissions to form $^{A-4}_{Z}M$.

2. The number of neutrons in the parent nucleus which gives ^{14}N on β-emission is __________.

3. The number of β-particles emitted in the reaction $^{239}_{94}Pu \rightarrow {}^{206}_{82}Pb + \alpha + \beta + {}^{1}_{0}n$ is __________.

4. Radioactive isotope A undergoes simultaneous decay into two different nuclei as



Assume that initially neither P nor Q were present, and calculate the time after which the amount of Q doubles that of A.

Matrix–Match Type

1. Match the nuclei with their correct designation.

Column I	Column II
(A) Isotopes	(p) $^{40}_{20}Ca$ and $^{40}_{19}Kr$
(B) Isotones	(q) $^{16}_{8}O$ and $^{17}_{8}O$
(C) Isobars	(r) $^{2}_{1}H$ and $^{3}_{2}He$
(D) Isosteres	(s) $^{39}_{19}K$ and $^{19}_{9}F$
(E) Isodiaphers	(t) CO_2 and N_2O

2. Match the process with the application.

Column I	Column II
(A) Carbon dating	(p) Atom bomb
(B) ^{60}Co	(q) Hydrogen bomb
(C) Nuclear fission	(r) Animals and plants
(D) Nuclear fusion	(s) Radio therapy

3. Match the nuclei/reaction with the process involved.

Column I	Column II
(A) $^{235}_{92}U$	(p) α-decay
(B) $^{23}_{11}Na + {}^{1}_{0}n \rightarrow {}^{24}_{12}Mg + {}^{0}_{-1}e^{-}$	(q) β-decay
(C) $^{9}_{5}B$	(r) Positron emission
(D) $^{226}_{88}Ra$	(s) Artificial radioactivity
	(t) Electron capture

ANSWERS

Review Questions

3. $^{16}_{8}\text{O}$, $^{17}_{8}\text{O}$ and $^{198}_{78}\text{Pt}$, $^{192}_{78}\text{Pt}$ are the isotope pairs; $^{14}_{7}\text{N}$, $^{14}_{6}\text{C}$ and $^{40}_{20}\text{Ca}$, $^{40}_{18}\text{Ar}$ are isobar pairs.

7. The element is Pb with mass number 206 and atomic number 82.

8. This is because the neutron is neutral.

9. **(a)** $7\,^{1}_{0}n$ **(b)** $^{86}_{36}\text{Kr}$

10. This is because they cannot penetrate tissues.

12. Increase; below

13. **(a)** ^{140}Ba **(b)** ^{112}Tin **(c)** ^{139}La

20. Electron capture is the more likely event: $^{37}_{18}\text{Ar} + \,^{0}_{-1}e \rightarrow \,^{37}_{17}\text{Cl}$

23. Gain or loss of neutrons interconverts isotopes, responses (e) and (f), and (g). Gain or loss of β-particles interconverts isobars, responses (a), (b), and (c). None of these interconvert isotones.

25. $^{40}\text{K}^{+}$: 18 electrons, 19 protons and 21 neutrons; $^{127}\text{I}^{-}$: 54 electrons, 53 protons and 74 neutrons

Numerical Problems

1. 14422 years
2. 8.526 MeV; 1.36×10^{-12} J
3. 4.95 MeV
4. 7.99 MeV
5. 4.2×10^{4} years
6. 1.90×10^{3} years
7. 746
8. 55.0 min
9. 144
10. 1.129×10^{-23}
11. 1×10^{5} kJ (mol photons)$^{-1}$
12. 4.65×10^{-4}
13. 2.16×10^{9} atoms min^{-1}
14. 6.3 m
15. **(a)** $^{198}_{79}\text{Au} \xrightarrow{-\beta} \,^{198}_{80}\text{Hg}$; **(b)** 0.9375 g
16. 0.62 MeV
17. 24.33
18. 1597.98 years
19. 7, 4
20. 6288 years old
21. **(a)** 8.9×10^{4} Ci; **(b)** 27.3 Ci; **(c)** 6.34×10^{-8} Ci
22. 1.38×10^{-11} s^{-1}; 3181 years
23. 7, 6
24. **(a)** 0.25; **(b)** 0.21
25. 49.85 h
26. 32.03 MeV atom^{-1}; 5.338 MeV nucleon^{-1}
27. 0.731 MeV
28. 206, 82
29. –3.18 ng; 1.77×10^{-8}%
30. 75 min
31. 5.62×10^{-10} g remaining
32. 1.8×10^{-13} J per nucleon
33. 3.2 rm
34. 2.4×10^{7} Bq or 6.5×10^{2} μCi
35. **(a)** $^{15}_{7}\text{N}$; **(b)** 140 mg
36. 1.39×10^{-8} g
37. 2.27×10^{9}
38. 2087109.82

Additional Objective Questions

Single Correct Choice Type

1. (B)
2. (D)
3. (D)
4. (A)
5. (C)
6. (B)
7. (A)
8. (C)
9. (A)
10. (D)
11. (C)
12. (D)
13. (C)
14. (C)
15. (A)
16. (B)
17. (B)
18. (C)
19. (D)
20. (C)
21. (C)
22. (C)
23. (B)
24. (C)
25. (D)
26. (D)
27. (C)
28. (C)
29. (C)
30. (C)
31. (A)
32. (C)
33. (B)
34. (B)
35. (D)
36. (A)
37. (D)
38. (D)
39. (B)
40. (B)
41. (B)
42. (C)
43. (C)

Multiple Correct Choice Type

1. (A, C)
2. (A, B)
3. (A, B, C)
4. (A, B, C)
5. (A, C)
6. (A, C)
7. (A, C, D)
8. (A, B)
9. (C, D)
10. (A, C)
11. (B, C)
12. (B, C)
13. (A, D)
14. (C, D)
15. (A, C)
16. (C, D)
17. (B, D)
18. (B, D)

Assertion–Reasoning Type

1. (B) **2.** (A) **3.** (A) **4.** (A)

Comprehension Type

1. (D) **2.** (A) **3.** (D) **4.** (C) **5.** (C)
6. (B) **7.** (B) **8.** (B) **9.** (B) **10.** (A)
11. (B) **12.** (C) **13.** (D) **14.** (A)

Integer Answer Type

1. (2) **2.** (8) **3.** (4) **4.** (5)

Matrix–Match Type

1. $A \to (q); B \to (r); C \to (p), D \to (t); E \to (s)$ **2.** $A \to (r); B \to (s); C \to (p), D \to (q)$
3. $A \to (p, q); B \to (s); C \to (r, t), D \to (p, q)$

APPENDIX

A

Chapter-wise Tests

INSTRUCTIONS

This question paper consists of **five types** of questions (Single Correct Choice, Multiple Correct Choice, Assertion-Reasoning, Comprehension and Matrix-Match). The marking scheme is

1. **For Single Correct Choice Type:** Three (3) marks for positive response and –1 mark for negative response.
2. **For Multiple Correct Choice Type:** Four (4) marks for positive response and –1 mark for negative response.
3. **For Assertion-Reasoning Type:** Four (4) marks for positive response and –1 mark for negative response.
4. **For Matrix Match Type:** Eight (8) marks for positive response and no negative marking for negative response.
5. **For Comprehension Type:** Four (4) marks for positive response and –1 mark for negative response.

MOLE CONCEPT–I

Single Correct Choice Type

1. 510 mg of liquid on vaporization in Victor Meyer's apparatus displaces 67.2 cm^3 of air at (STP). The molecular weight of the liquid is

(A) 130
(B) 17
(C) 170
(D) 1700

2. 1.84 g mixture of $CaCO_3$ and $MgCO_3$ on heating gives CO_2. Volume of CO_2 obtained is measured to be 448 mL at STP. Mass of $CaCO_3$ in the mixture is

(A) 0.5 g
(B) 0.84 g
(C) 0.92 g
(D) 1.00 g

3. Phosphine (PH_3) decomposes to produce P_4 (g) and H_2 (g). What would be the change in volume when 100 mL of PH_3(g) is completely decomposed?

(A) 50 mL
(B) 500 mL
(C) 75 mL
(D) 250 mL

4. The density of 2.45 M methanol solution in water is 0.9766 g mL^{-1}. The molality of the solution is

(A) 27.3
(B) 2.73
(C) 2.45
(D) 0.273

5. Density of 3M Na_2CO_3 solution in water is 1.2 g mL^{-1}. The percentage by weight and ppm of Na_2CO_3 are respectively,

(A) 26.5 and 2.65×10^5

(B) 2.65 and 2.65×10^4

(C) 265 and 2.65×10^3

(D) 5.23 and 2.65×10^6

6. 100 mL of CH_4 and C_2H_2 were exploded with excess of O_2. After explosion and cooling, the mixture was treated with KOH, where a reduction of 165 mL was observed. Therefore the composition of the mixture is

(A) $CH_4 = 35$ mL; $C_2H_2 = 65$ mL

(B) $CH_4 = 65$ mL; $C_2H_2 = 35$ mL

(C) $CH_4 = 75$ mL; $C_2H_2 = 25$ mL

(D) $CH_4 = 25$ mL; $C_2H_2 = 75$ mL

7. A mixture of CO and CO_2 having a volume of 20 mL is mixed with x mL of oxygen and electrically sparked. The volume after explosion is $(16 + x)$ mL under the same conditions. What would be the residual volume if 30 mL of the original mixture is treated with aqueous NaOH?

(A) 12 mL (B) 10 mL

(C) 9 mL (D) 8 mL

8. The mass of oxygen that would be required to produce enough CO, which completely reduces 1.6 kg Fe_2O_3 (at. mass of Fe = 56) is

$$(Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2)$$

(A) 240 g (B) 480 g

(C) 720 g (D) 960 g

9. Calculate the weight of lime (CaO) obtained by heating 200 kg of 95% pure limestone ($CaCO_3$).

(A) 104.4 kg (B) 105.4 kg

(C) 212.8 kg (D) 106.4 kg

10. The mole fraction of a given sample of I_2 in C_6H_6 is 0.2. The molality of I_2 in C_6H_6 is

(A) 0.32 (B) 3.2

(C) 0.032 (D) 0.48

11. Haemoglobin contains 0.33% of iron by weight. The molecular weight of haemoglobin is approximately 67200. The number of iron atoms (at. mass of Fe = 56) present in one molecule of haemoglobin are

(A) 1 (B) 2

(C) 4 (D) 6

Multiple Correct Choice Type

12. 11.2 g of mixture of MCl (volatile) and NaCl gave 28.7 g of white precipitate with excess of $AgNO_3$ solution. 11.2 g of the same mixture on heating gave a gas that on passing into $AgNO_3$ solution gave 14.35 g of white precipitate Hence

(A) ionic mass of M^+ is 18.

(B) mixture has equal mole fraction of MCl and NaCl.

(C) MCl and NaCl are in 1: 2 molar ratio.

(D) ionic mass of M^+ is 10.

13. Which of the following compounds has the same percentage of carbon as in ethane?

(A) 2-Butene

(B) Cyclohexane

(C) Cyclohexene

(D) 2-Methyl but-2-ene

14. 10 g of a sample of silver which is contaminated with silver sulphide produced 11.2 mL of hydrogen sulphide at STP by treatment with excess of hydrochloric acid. The mass of silver sulphide in the sample is (at. mass of Ag = 108; S = 32)

(A) 1.24 g (B) 124 mg

(C) 5×10^{-4} mol (D) 62 g

15. 2.0 g of a triatomic gaseous element was found to occupy a volume of 448 mL at 76 cm of Hg and 273 K. The mass of its atom is

(A) 33.3 amu (B) 5.53×10^{-23} g

(C) 33.3 g (D) 5.53 amu

16. 2.4 g of pure Mg (at. mass 24) is dropped in 100 mL of 1N HCl. Which of the following statements are correct?

(A) 1.122 L of hydrogen is produced at STP.

(B) 0.01 mol of magnesium is left behind.

(C) 0.1 mol of Mg^+ ions are formed in solution.

(D) HCl is the limiting reagent.

Assertion-Reasoning Type

Choose the correct option from the following:

(A) Statement 1 and Statement 2 are True, Statement 2 is the correct explanation of the Statement 1.

(B) Statement 1 and Statement 2 are True, Statement 2 is NOT a correct explanation of the Statement 1.

(C) Statement 1 is True, Statement 2 is False.

(D) Statement 1 is False, Statement 2 is True.

17. **Statement 1:** Molality (m) of a solution is related with molarity (M) of solution

$$\frac{1}{M} = \frac{1}{d}\left\{\frac{1}{m} + \frac{M_1}{1000}\right\}$$

Here, d = density of solution in g mL^{-1}

M_1 = molar mass of solute.

Statement 2: Molality of a solution is equal to number of moles of solute dissolved in 1 kg of solution.

18. **Statement 1:** Vapor density of sulphur vapor relative to oxygen is 2 because sulphur atom is twice as heavy as that of O atom.
Statement 2: Vapor density depends upon the molecular state of the substance.

19. **Statement 1:** Equal volumes of all the gases contain equal number of atoms.
Statement 2: Atom is the smallest particle which takes part in chemical reactions.

Comprehension Type

Paragraph I

Questions given below are based on two industrial observations:

(i) Phosphoric acid H_3PO_4, is widely used to make fertilizer and can be prepared by a two-step process

Step I: $P_4 + 5O_2 \rightarrow P_4O_{10}$
Step II: $P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$

We allow 310 g of phosphorus to react with excess oxygen, which forms tetraphosphorous dioxide P_4O_{10}, in 50% yield. In step II reaction 25% yield of H_3PO_4 is obtained.

(ii) In order to remove organic sulphur from coal, the following reactions are carried out.

$$X\text{–}S\text{–}Y + 2\,NaOH \rightarrow X\text{–}O\text{–}Y + Na_2S + H_2O$$
$$CaCO_3 \rightarrow CaO + CO_2$$
$$Na_2S + CO_2 + H_2O \rightarrow Na_2CO_3 + H_2S$$
$$CaO + H_2O \rightarrow Ca(OH)_2$$
$$Na_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3 + 2NaOH$$

20. Assuming 100% yield, the number of moles of H_3PO_4 that would be obtained is

(A) 1.25 (B) 10.0

(C) 5.0 (D) 2.5

21. Actual number of moles of H_3PO_4 obtained in experimental conditions is

(A) 5 (B) 2.5

(C) 1.25 (D) 0.3125

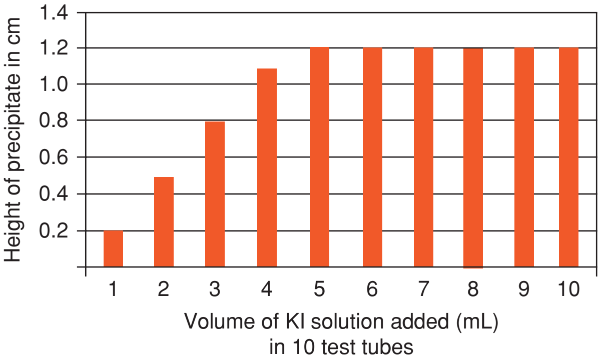
22. In processing of 200 kg of coal having 4% sulphur content, the weight of limestone that must be decomposed to provide enough $Ca(OH)_2$ to regenerate the NaOH used in the original leaching step is

(A) 6.25 kg (B) 12.5 kg

(C) 18.75 kg (D) 25 kg

Paragraph II

The following chart shows the height of a secret metal iodide precipitate that was formed in a series of 10 test tubes. Each test tube contained 3.0 mL of a metal nitrate solution (1.0 mol L^{-1} with respect to the metal ions). Measured volumes of 1.0 mol L^{-1} potassium iodide (KI) solution were added to each tube in turn to form the precipitate.



23. What is the formula of the metal iodide according to this chart?

(A) MI_4 (B) MI

(C) MI_2 (D) MI_3

24. If the height of precipitate in test tubes 4 and 6 are considered to be authentic, then which test tubes are reporting wrong height of precipitate?

(A) 1 and 2 (B) 2 and 3

(C) 2 and 5 (D) 5, 7, 8, 9 and 10

25. The molarity of I^- (aq) ion in the ninth test tube is

(A) 1.0 M (B) 0.5 M

(C) 0.33 M (D) 0.25 M

26. The constant heights of precipitates after addition of 6.0 mL or higher volume of KI solution indicates that

(A) the solution has become saturated in KI.

(B) the weighing limit of balance has been exceeded.

(C) the entire metal ion has been precipitated out.

(D) the information available is insufficient to interpret this observation.

Matrix-Match Type

27. Match the description with the concentration term.

Column I	Column II
(A) Concentration units(s) independent of temperature variation	(p) Molality
(B) Concentration units(s) dependent on temperature variation	(q) Molarity
(C) mg of solute present in 1 kg of solution	(r) ppm concentration
(D) moles of solute present in 1 kg of solvent	(s) moles of solute in hundred moles of solution

28. Match the compound with the observation

Column I	Column II
(A) On decomposition, 50% increase in volume at the same temperature and pressure	(p) NH_3
(B) On decomposition, 100% increase in volume at the same temperature and pressure	(q) HCl
(C) On decomposition no change in volume at the same temperature and pressure	(r) O_3
(D) Gases highly soluble in water	(s) HBr

MOLE CONCEPT–II

Single Correct Choice Type

1. In Mohr salt, oxidation number of N is

(A) –3 (B) –2

(C) +1 (D) +5

2. The oxidation number of S in $S_2O_8^{2-}$ is

(A) –7 (B) +7

(C) +6 (D) –6

3. What weight of nitrate ion (calculated as HNO_3) is needed to convert 5 g of iodine into iodic acid according to the following reaction?

$$I_2 + HNO_3 \longrightarrow HIO_3 + NO_2 + H_2O$$

(A) 12.4 g (B) 24.8 g

(C) 0.248 g (D) 49.6 g

4. During the oxidation of arsenite to arsenate ion in alkaline medium, the number of moles of hydroxide ions involved per mole of arsenite ion is

(A) 2 (B) 3

(C) 2/3 (D) None of these

5. What is the equivalent weight of HNO_3 in the following reaction?

$$4Zn + 10HNO_3 \rightarrow 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O$$

(A) $\frac{63}{10}$ (B) $\frac{63}{9}$

(C) $\frac{63}{8} \times 10$ (D) $\frac{63}{4} \times 14$

6. What is the equivalent weight of $C_{12}H_{22}O_{11}$ in the following reaction?

$$C_{12}H_{22}O_{11} + 36HNO_3 \rightarrow 6H_2C_2O_4 + 36NO_2 + 23H_2O$$

(A) $\frac{342}{36}$ (B) $\frac{342}{12}$

(C) $\frac{342}{22}$ (D) $\frac{342}{3}$

7. Equivalent weight of H_3PO_2 when it disproportionate into PH_3 and H_3PO_3 is (mol. wt. of $H_3PO_2 = M$)

(A) M (B) $\frac{3M}{4}$

(C) $\frac{M}{2}$ (D) $\frac{M}{4}$

8. The equivalent weight of $Fe_2(SO_4)_3$, the salt to be used as an oxidant in an acid solution, is

(A) (mol. wt.)/1
(B) (mol. wt.)/2
(C) (mol. wt.)/3
(D) (mol. wt.)/5

9. RH_2 (ion exchange resin) can replace Ca^{2+} in hard water as

$$RH_2 + Ca^{2+} \longrightarrow RCa + 2H^+$$

1 L of hard water after passing through RH_2 has pH 2. Hence, hardness in ppm of Ca^{2+} is

(A) 200
(B) 100
(C) 50
(D) 125

10. 200 mL of hard water was boiled with 100 mL of *N*/50 Na_2CO_3 reagent. After boiling, the solution was again made to 200 mL and filtered. 25 mL of the filtrate required 8.2 mL of *N*/50 HCl for neutralization. The permanent hardness of given hard water sample is

(A) 172 ppm
(B) 86 ppm
(C) 344 ppm
(D) 400 ppm

11. In the mixture of $NaHCO_3$ and Na_2CO_3, volume of given HCl required for neutralization is x mL with phenolphthalein indicator and further y mL is required with methyl orange indicator. Hence, volume of HCl for complete reaction of $NaHCO_3$ is

(A) $2x$
(B) y
(C) $\frac{x}{2}$
(D) $(y - x)$

12. 40 mL of 0.05 M solution of sodium sesquisesqicarbonate ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$) is titrated against 0.05 M HCl. x mL of HCl is used when phenolphthalein is the indicator and y mL of HCl is used when methyl orange is the indicator in two separate titrations. Hence, $(y - x)$ is

(A) 80 mL
(B) 30 mL
(C) 120 mL
(D) 90 mL

13. Mass of KHC_2O_4 (potassium acid oxalate) required to reduce 100 mL of 0.02 M $KMnO_4$ in acidic medium (to Mn^{2+}) is x g and to neutralize 100 mL of 0.05 M $Ca(OH)_2$ is y g, then

(A) $x = y$
(B) $2x = y$
(C) $x = 2y$
(D) $3x = y$

14. During the disproportionation of I_2 to iodide and iodate ions, the ratio of iodate and iodide ions formed in alkaline medium is

(A) 1: 5
(B) 5: 1
(C) 3: 1
(D) 1: 3

15. For the redox reaction

$$MnO_4^- + C_2O_4^{2-} + H^+ \longrightarrow Mn^{2+} + CO_2 + H_2O$$

the correct coefficients of the reactants for the balanced reaction are

	MnO_4^-	$C_2O_4^{2-}$	H^+
(A)	2	5	16
(B)	16	5	2
(C)	5	16	2
(D)	2	16	5

Multiple Correct Choice Type

16. The oxidation number of Cr = +6 in

(A) $FeCr_2O_4$
(B) $KCrO_3Cl$
(C) CrO_5
(D) $[Cr(OH)_4]^-$

17. Which of the following have been arranged in order of decreasing oxidation number of sulphur?

(A) $H_2S_2O_7 > Na_2S_4O_6 > Na_2S_2O_3 > S_8$
(B) $SO^{2+} > SO_4^{2-} > SO_3^{2-} > HSO_4^-$
(C) $H_2SO_5 > H_2SO_3 > SCl_2 > H_2S$
(D) $H_2SO_4 > SO_2 > H_2S > H_2S_2O_8$

18. Which of the following are primary standard substances?

(A) $Na_2CO_3 \cdot 10H_2O$
(B) NaOH
(C) $Na_2B_4O_7 \cdot 10H_2O$
(D) $KMnO_4$

19. 20 volumes of H_2O_2 is equal to

(A) 20% H_2O_2 by mass.
(B) 6% H_2O_2 by mass.
(C) 1.764 N
(D) 3.528 N

20. A solution of $Na_2S_2O_3$ is standardized iodometrically against 0.1262 g of $KBrO_3$. This process requires 45 mL of the $Na_2S_2O_3$ solution. What is the strength of the $Na_2S_2O_3$?

(A) 0.2 M
(B) 0.1 M
(C) 0.05 N
(D) 0.1 N

Assertion-Reasoning Type

Choose the correct option from the following:

(A) Statement 1 and Statement 2 are True, Statement 2 is the correct explanation of the Statement 1.

(B) Statement 1 and Statement 2 are True, Statement 2 is NOT a correct explanation of the Statement 1.

(C) Statement 1 is True, Statement 2 is False.

(D) Statement 1 is False, Statement 2 is True.

21. **Statement I:** $KClO_3$ is a strong oxidizing agent.

Statement II: Chlorine present in $KClO_3$ is highly electronegative.

22. **Statement I:** $ZnSO_4{\cdot}7H_2O$ and $FeSO_4{\cdot}7H_2O$ are isomorphous.

Statement II: Compounds with similar chemical composition and same crystalline forms are called isomorphous.

23. **Statement I:** For most of the solid elements, atomic weights are related to their specific heats.

Statement II: Greater the specific heat, less is the atomic mass.

Comprehension Type

Paragraph I

When ammonium vanadate is heated with oxalic acid solution a compound Z is formed. A sample of Z was titrated with $KMnO_4$ in hot acidic solution. The resulting liquid was reduced with SO_2, the excess of SO_2 is boiled off and liquid again titrated with $KMnO_4$. The ratio of the volumes of $KMnO_4$ used in two titrations was 5 : 1. $KMnO_4$ oxidizes all oxidation states of vanadium to vanadium (+V) and SO_2 reducess vanadium (+V) to vanadium (+IV).

24. What is the oxidation state of vanadium in the compound Z?

(A) +2
(B) +1
(C) 0
(D) −1

25. If vanadium exists as VO_4^{3-}, species reduced by SO_2 would be

(A) VO_4^{2-}
(B) VO_3^{2-}
(C) VO_2^{2-}
(D) VO^{2-}

26. Consider following redox reaction:

$$VO_3^{2-} + MnO_4^- \rightarrow Mn^{2+} + VO_4^{3-}$$

1 mol of VO_3^{2-} is oxidized by x mol of MnO_4^-. Thus, x is,

(A) 0.2
(B) 0.4
(C) 0.8
(D) 1.0

27. Number of moles of MnO_4^- required to titrate 1 mol of Z in hot acidic solution is

(A) 0.2
(B) 0.4
(C) 0.8
(D) 1.0

28. Compound Z is

(A) VO_4^{3-}
(B) VO_3^{2-}
(C) V (Vanadium)
(D) VO_2^{2+}

Paragraph II

Chromium exists as $FeCr_2O_4$ in nature and it contains $Fe_{0.95}O$ and other impurities. To obtain pure chromium from $FeCr_2O_4$, the ore is fused with KOH and oxygen is passed through the mixture when K_2CrO_4 and Fe_2O_3 are produced.

$$FeCr_2O_4 + KOH + O_2 \rightarrow K_2CrO_4 + Fe_2O_3$$

$$Fe_{0.95}O + O_2 \rightarrow Fe_2O_3$$

2 g of ore required 270 mL of O_2 at 273 K and 1 atm for complete oxidation of ore. K_2CrO_4 is precipitated as $BaCrO_4$ when barium salt is added. To the remaining solution, 10 mL of 1 M $K_4[Fe(CN)_6]$ is added when Fe^{3+} ions react with it to form $K_2Fe[Fe(CN)_6]$, often called 'Prussian blue'. To determine excess of $K_4[Fe(CN)_6]$ in solution, 7 mL of 0.2 N of Fe^{2+} is added when all the $K_4[Fe(CN)_6]$ is precipitated as $K_2Fe[Fe(CN)_6]$.

29. Weight of $BaCrO_4$ precipitated is

(A) 1.64
(B) 6.29
(C) 0.82
(D) 3.29

30. % by mass of $Fe_{0.95}O$ in the ore is

(A) 9.6%
(B) 10.1%
(C) 8.55%
(D) 20.2%

31. n factor for $Fe_{0.95}O$ is

(A) 0.9
(B) 0.85
(C) $\dfrac{2}{0.95}$
(D) 1.8

32. Weight of impurities present in the ore is

(A) 0.421 (B) 0.123

(C) 0.341 (D) 0.206

Paragraph III

A steel sample is to be analyzed for Cr and Mn simultaneously. By suitable treatment, Cr is oxidized to $Cr_2O_7^{2-}$ and the Mn to MnO_4^-.

$$Cr \rightarrow Cr_2O_7^{2-}$$

$$Mn \rightarrow MnO_4^-$$

A 10 g sample of steel is used to produce 250 mL of a solution containing $Cr_2O_7^{2-}$ and MnO_4^-. A 10 mL portion of this solution is added to a $BaCl_2$ solution and by proper adjustment of the acidity, the chromium is completely precipitated as $BaCrO_4$, 0.0549 g is obtained.

$$Cr_2O_7^{2-} \xrightarrow{H^+} BaCrO_4$$

A second 10 mL portion of this solution requires exactly 15.95 mL of 0.0750 M standard Fe^{2+} solution for its titration (in acid solution).

33. % of chromium in the steel sample is

(A) 1.496 (B) 2.82

(C) 1.96 (D) 5

34. Equivalent of Fe^{2+} required for reduction of MnO_4^- is

(A) 5.44×10^{-4} (B) 0.544×10^{-2}

(C) 1.196×10^{-3} (D) 11.96×10^{-4}

35. Amount of $BaCl_2$ required for conversion of $Cr_2O_7^{2-}$ to $BaCrO_4$ in steel sample is

(A) 0.045 (B) 0.0549

(C) 1.125 (D) 2.82

Matrix-Match Type

36. Match the element with its oxidation number.

Column I	Column II
(A) P in $Na_4P_2O_7$	(p) +2
(B) O in $O_2[PtF_6]$	(q) −3, +5
(C) Fe in FeO	(r) +5
(D) S in H_2SO_5	(s) +1/2
(E) N in NH_4NO_3	(t) +6

37. Match the characteristic property with its elements/compounds.

Column I	Column II
(A) Nitrogen shows oxidation number	(p) Itself reduces
(B) Oxygen family except oxygen shows oxidation number	(q) −2 to +6
(C) Carbon shown oxidation number	(r) −4 to +4
(D) MnO_4^-	(s) −3 to +5
(E) $C_2O_4^{2-}$	(t) Oxidizes itself

GASEOUS AND LIQUID STATE

Single Correct Choice Type

1. In the figures below a doll is entrapped within a piston and cylinder containing gas. Initial and final conditions are shown Fig. I and Fig. II respectively. The volume of doll is

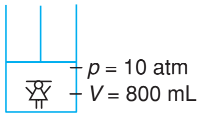


Figure I

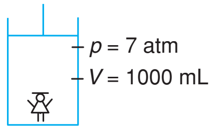


Figure II

(A) 1000 mL (B) $\frac{15000}{17}$ mL

(C) $\frac{1000}{3}$ mL (D) $\frac{1000}{15}$ mL

2. In Fig. I below an air column of length l_1, is entrapped by a column of Hg of length 8 cm. In Fig. II, the length of the same air column at the same temperature is l_2. Then l_1/l_2 is (1 atm = 76 cm of Hg)

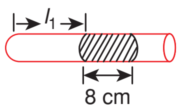


Figure I

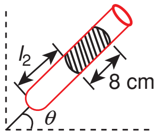


Figure II

(A) $1+\frac{2}{19}\times\cos\theta$ (B) $1+\frac{2}{19}\times\sin\theta$

(C) $1+\frac{2}{21}\times\sin\theta$ (D) $\frac{21}{19}$

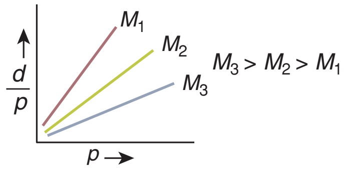
3. To determine the value of R, which of the following pV value is considered to be equal for every gas at 273 K?

(A) $\lim_{p\to 1\text{atm}}(pV_m)$ (B) $\lim_{p\to 0}(pV_m)$

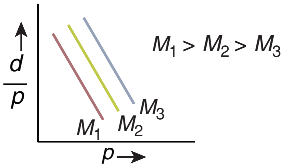
(C) $\lim_{p\to \infty}(pV_m)$ (D) $\lim_{V\to 0}(pV_m)$

4. For the different ideal gases (d/p) versus p variations at definite temperature is

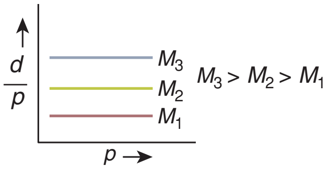
(A)



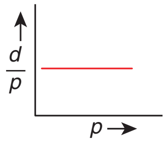
(B)



(C)



(D)



5. To a given container having a pore of definite size, gas A (mol. wt. = 81) is filled till the final pressure becomes 10 atm. It was seen that in 50 min, 10 g of A effused out. Now the container was completely evacuated and filled with gas B (mol. wt. = 100) till the final pressure become 20 atm. In 75 min, how many grams of B will be effused out?

(A) $\frac{100}{6}$ g (B) $\frac{100}{3}$ g

(C) $\frac{200}{3}$ g (D) $\frac{250}{3}$ g

6. Regarding the van der Waals constant, which of the following is/are correct?

(A) a depends on the intermolecular interactions.

(B) b depends on the size of the gas molecules.

(C) a and b are the characteristic constants not the universal gas constant.

(D) All of the above are correct.

7. Regarding compressibility factor Z, which of the following is/are correct?

(A) For most of the real gases, Z decreases with p at the lower pressure.

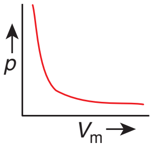
(B) For most of the real gases, Z increases with p at the higher pressure.

(C) For $H_2(g)$ and He(g), Z increases with p at all the pressures and at room temperature.

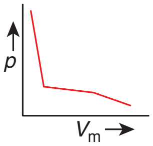
(D) All of the above are correct.

8. Below the critical temperature, which of the following represent van der Waals gas?

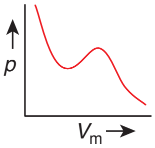
(A)



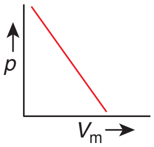
(B)



(C)



(D)



9. Which of the following statements characterizes the critical point?

(A) At the critical point, both liquid and solid phases coexist.

(B) At the critical point, solid, liquid and gas phases coexist.

(C) At the critical point, liquid and gas phases coexist.

(D) At the critical point, liquid and gas phases have unequal density.

10. Critical temperature (T_c) and critical pressure (p_c) values of four gases are given below.

Gas	T_c (K)	p_c (atm)
P	5.1	2.2
Q	33	13
R	126	34
S	135	40

Which of the gas/gases cannot be liquefied at a temperature 100 K and pressure 50 atm?

(A) S only (B) P only

(C) R and S (D) P and Q

11. A certain gas effuses out of two different vessels A and B. A has a circular orifice while B has a square orifice of length equal to the radius of the orifice of vessel A. The ratio of rate of diffusion of the gas from vessel A to that from vessel B is

(A) $\pi:1$ (B) $1:\pi$

(C) $1:1$ (D) $3:2$

12. A balloon with volume 4200 m^3 is filled with helium gas at 27ºC, 1 bar pressure and is found to weigh 700 kg. If density of air is 1.2 kg m^{-3}, the payload of balloon is

(A) 5040 kg (B) 4340 kg

(C) 3500 kg (D) 5740 kg

13. Two glass bulbs A (of 100 mL capacity), and B (of 150 mL capacity) containing the same gas are connected by a small tube of negligible volume. At particular temperature, the pressure before opening the valve $\frac{p_A}{p_B} = \frac{20}{1}$. The stopcock is opened without changing the temperature. The pressure in A will

(A) drop by 75%. (B) drop by 57%.

(C) drop by 25%. (D) will remain the same.

14. van der Waals constant b and the corresponding values of critical temperature for three gases P, Q, R are given below:

Gas	Critical temperature (T_c)	van der Waal's constant (b)
P	–200ºC	0.03 L mol^{-1}
Q	–100ºC	0.02 L mol^{-1}
R	+50ºC	0.01 L mol^{-1}

Which of the gas/gases is/are liquefiable at a temperature –110ºC by application of increasing pressure?

(A) P, Q, R (B) P, Q

(C) Q, R (D) None of P, Q, R

15. NH_3 gas is liquefied more easily than N_2. Hence,

(A) van der Waals constants a and b of NH_3 are greater than that of N_2.

(B) van der Waals constants a and b of NH_3 are lower than that of N_2.

(C) $a(NH_3) > a(N_2)$ but $b(NH_3) < b(N_2)$.

(D) $a(NH_3) < a(N_2)$ but $b(NH_3) > b(N_2)$.

Multiple Correct Choice Type

16. Four gas balloons A, B, C, D of equal volumes containing, H_2, N_2O, CO, CO_2, respectively were pricked with needle and immersed in a tank containing CO_2. Which of them will shrink after some time?

(A) A (B) B

(C) C (D) Both A and D

17. According to Maxwell–Boltzmann distribution of speeds among gas molecules, which of the following statements are incorrect?

(A) The maxima in plot of $\frac{\Delta N}{N}$ vs. speed pertains to average speed.

(B) The plot of $\frac{\Delta N}{N}$ vs. speed is a straight line with slope > 0.

(C) The value of root mean square velocity increases with rise in temperature.

(D) Area under the curve gives the total number of molecules.

18. Which of the following are not correctly matched with the value of van der Waal constant a?

(A) C_6H_6 (g); $a = 0.217$

(B) $C_6H_5CH_3$(g); $a = 18$

(C) Ne; $a = 5.464$

(D) H_2O(g); $a = 24.06$

Assertion-Reasoning Type

Choose the correct option from the following:

(A) Statement 1 and Statement 2 are True, Statement 2 is the correct explanation of the Statement 1.

(B) Statement 1 and Statement 2 are True, Statement 2 is NOT a correct explanation of the Statement 1.

(C) Statement 1 is True, Statement 2 is False.

(D) Statement 1 is False, Statement 2 is True.

19. **Statement 1:** At a particular temperature, the value of mean free path increases with decrease in pressure.

Statement 2: All the gas molecules at a particular temperature possess same speed.

20. **Statement 1:** Noble gases can be liquefied.

Statement 2: Attractive forces can exist between non-polar molecules.

Comprehension Type

Paragraph I

Under a given condition, it is found that two separate gases (gas I and gas II) effuse out of two separate containers in such a way that they follow the equation

$$\frac{dN}{dt} = -k_1 N \text{ and } \frac{dN}{dt} = -k_2 N,$$

where $k_1 = 6.93 \times 10^{-3}\ s^{-1}$, $k_2 = 6.93 \times 10^{-5}\ s^{-1}$, and N is the number of molecules remaining in the container.

21. Which of the following may represent fraction of molecules present after the given interval for gas I?

	$t = 0$	$t = 100$ s	$t = 200$ s
(A)	1	$\frac{1}{2}$	$\frac{1}{8}$
(B)	1	$\frac{1}{8}$	$\frac{1}{16}$
(C)	1	$\frac{1}{2}$	$\frac{1}{4}$
(D)	1	$\frac{1}{4}$	$\frac{1}{16}$

22. Identify the correct option regarding sequence of True (T) and False (F) statements.

(i) The time required for number of moles of gas I to get reduced to half of original and that of gas II to reduced to half of original is independent of initial number of moles of gas I and gas II.

(ii) The rate at which initially molecules will effuse out in gas I will be greater as compared to gas II, if initial number of molecules is same.

(iii) The time required for number of moles to get reduced from 1 to 0.8 in gas I and 2 to 1.6 in gas II will be the same.

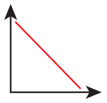
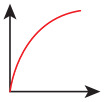
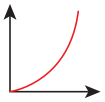
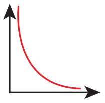
(iv) For the two gases, number of moles remaining in the container after same interval should be in geometrical progression.

(A) TFFT (B) TFTT

(C) FTFT (D) TTFF

Matrix-Match Type

23. Match the description with its characteristic curve.

Column I	Column II
(A) $\frac{1}{V^2}$ vs. p for ideal gas at constant T and n	(p) 
(B) V vs. $\frac{1}{T}$ for ideal gas at constant p and n	(q) 
(C) $\log p$ vs. $\log V$ for ideal gas at constant T and n	(r) 
(D) V vs. $\frac{1}{p^2}$ for ideal gas at constant T and n	(s) 

24. Match the term with its expression.

Column I	Column II
(A) $\left(p + \frac{a}{4V^2}\right) \times (2V - b) = RT$	(p) Real gas
(B) $\sqrt{\frac{3p}{d}}$	(q) van der Waals equation for 0.5 mol of gas
(C) $\frac{C_p}{C_V} = 1.66$	(r) Root mean square velocity
(D) $\frac{2a}{Rb}$	(s) Monoatomic gas
(E) $Z >$ or < 1	(t) Inversion temperature

SOLID STATE

Single Correct Choice Type

1. Consider cube 1 of body centered cubic unit cell of edge length a. Now atom at the body center can be viewed to be lying on the corner of another cube 2. Find the volume common to cube 1 and cube 2.

(A) $\frac{a^3}{27}$ (B) $\frac{a^3}{64}$

(C) $\frac{a^3}{2\sqrt{2}}$ (D) $\frac{a^3}{8}$

2. First three nearest neighbor distances for primitive cubic lattice are respectively (edge length of unit cell = a)

(A) $a, \sqrt{2}a, \sqrt{3}a$ (B) $\sqrt{3}a, \sqrt{2}a, a$

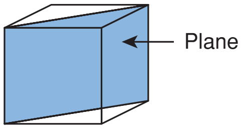
(C) $a, \sqrt{2}a, 2a$ (D) $a, \sqrt{3}a, 2a$

3. First three nearest neighbor distances for body centered cubic lattice are respectively,

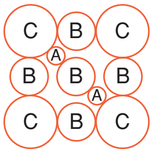
(A) $\sqrt{2}a, a, \sqrt{3}a$ (B) $\frac{a}{\sqrt{2}}, a, \sqrt{3}a$

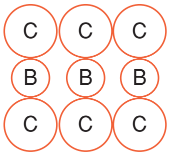
(C) $\frac{\sqrt{3}a}{2}, a, \sqrt{2}a$ (D) $\frac{\sqrt{3}a}{2}, a, \sqrt{3}a$

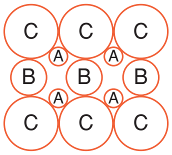
4. In a hypothetical solid C, atoms form ccp lattice with A atoms occupying all the tetrahedral voids and B atoms occupying all the octahedral voids. A and B atoms are of the appropriate size such that there is no distortion in the ccp lattice. Now if a plane is cut (as shown) then the cross section would like

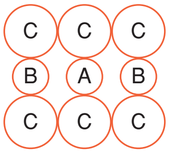


ccp unit cell

(A)


(B)


(C)


(D)


5. NiO adopts a rock-salt structure. The coordination number of the Ni^{2+} ion is

(A) two (B) four

(C) twelve (D) six

6. 8 : 8 coordination is noticed in

(A) MgO (B) Al_2O_3

(C) CsCl (D) All of the above

7. What type of crystal defect is indicated in the diagram below?

Na^+ Cl^- Na^+ Cl^- Na^+ Cl^-
Cl^- ☐ Cl^- Na^+ ☐ Na^+
Na^+ Cl^- ☐ Cl^- Na^+ Cl^-
Cl^- Na^+ Cl^- Na^+ ☐ Na^+

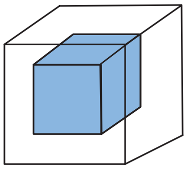
(A) Frenkel defect

(B) Schottky defect

(C) Interstitial defect

(D) Frenkel and Schottky defect

8. In an fcc unit cell, a cube is formed by joining the centers of all the tetrahedral voids to generate a new cube. Then the new cube would contain voids as



(A) 1 tetrahedral void, 1 octahedral void.

(B) 1 tetrahedral void only.

(C) 8 tetrahedral voids and 1 octahedral void.

(D) 1 octahedral void only.

9. $MgAl_2O_4$, is found in the spinel structure in which O^{2-} ions constitute ccp lattice, Mg^{2+} ions occupy 1/8th of the tetrahedral voids and Al^{3+} ions occupy 1/2 of the octahedral voids. Find the total positive charge contained in one unit cell.

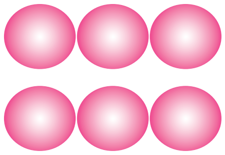
(A) +7/4 electronic charge

(B) +6 electronic charge

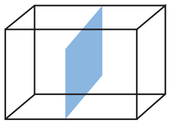
(C) +2 electronic charge

(D) +8 electronic charge

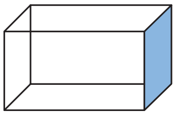
10. Which of the shaded planes in following fcc lattice contains arrangement of atoms as shown by circles?



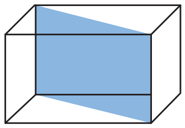
(A)



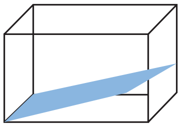
(B)



(C)



(D)



11. Cesium chloride on heating to 760 K changes into

(A) CsCl(s).

(B) NaCl structure.

(C) antifluorite structure.

(D) ZnS structure.

Multiple Correct Choice Type

12. Which of the following statements is/are incorrect about amorphous solids?

(A) They undergo clean cleavage.

(B) They do not have sharp melting points.

(C) They have high degree of rigidity.

(D) They exhibit isotropy.

13. Which of the following is/are likely to exhibit frenkel type defect?

(A) NaBr (B) ZnS

(C) AgBr (D) CsCl

14. What is/are true about diamagnetic materials?

(A) They are weakly repelled by the magnetic field.

(B) There are large number of unpaired electrons.

(C) They have all paired electrons.

(D) Benzene and TiO_2 are diamagnetic substances.

15. The ionic radii of Cs and Cl are 0.165 nm and 0.181 nm, respectively. Their atomic weights are 133 and 35.5. Then

(A) the lattice parameter is 0.4 nm.

(B) the lattice parameter cannot be determined from this data.

(C) the density of CsCl is 4.37×10^3 kg m^{-3}.

(D) CsCl has a fcc structure.

16. The coordination number of fcc structure for metals is 12, since

(A) each atom touches 4 others in the same layer, 3 in the layer above and 3 in the layer below.

(B) each atom touches 4 others in the same layer, 4 in the layer above and 4 in the layer below.

(C) each atom touches 6 others in the same layer, 3 in the layer above and 3 in the layer below.

(D) each atom touches 3 others in the same layer, 6 in the layer above and 6 in the layer below.

Assertion-Reasoning Type

Choose the correct option from the following:

(A) Statement 1 and Statement 2 are True, Statement 2 is the correct explanation of the Statement 1.

(B) Statement 1 and Statement 2 are True, Statement 2 is NOT a correct explanation of the Statement 1.

(C) Statement 1 is True, Statement 2 is False.

(D) Statement 1 is False, Statement 2 is True.

17. **Statement 1:** A particle present at the corner of the end centered unit cell has $\frac{1}{8}$th of its contribution to the unit cell.

Statement 2: In any space lattice, the corner of the unit cell is always shared by the eight unit cells.

18. **Statement 1:** An important feature of fluorite structures is that cations being large in size, occupy fcc lattice points whereas anions occupy all the tetrahedral voids giving the formula unit AB_2. (A: cation, B: anion.)

Statement 2: There are 6 cations and 12 anions per fcc unit cell of the fluorite structure.

19. **Statement 1:** In AgCl crystal, frenkel defect can be observed.

Statement 2: Ag^+ is a small sized cation.

Comprehension Type

Paragraph I

A metal crystallizes in a closed packed structure, the atoms stack together occupying maximum space and leaving minimum vacant space. Each sphere in the first layer is in contact with six neighbors. Now while arranging the second layer on the first layer, spheres are placed in depression of first layer. Spheres of third layer lie in the depression of second layer that do not lie directly over the atoms of first layer. This repeating arrangement of atoms produces a giant lattice.

20. If the edge length of unit cell is *a*, then what is the shortest distance between two atoms?

(A) $\frac{a}{2}$ (B) a

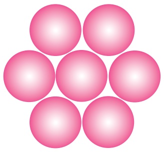
(C) $\frac{a}{\sqrt{2}}$ (D) $\frac{\sqrt{3}a}{4}$

21. If atomic weight of metal is 197 and $a = 4.07$Å, then density of unit cell is

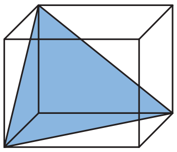
(A) 49.8 g cm^{-3} (B) 19.4 g cm^{-3}

(C) 56.2 g cm^{-3} (D) 86.5 g cm^{-3}

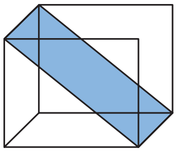
22. Which of the following shaded plane contains the following arrangement of atoms?



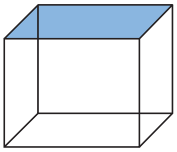
(A)



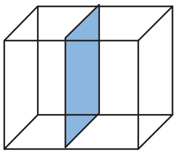
(B)



(C)



(D)



Paragraph II

Calcium crystallizes in a cubic unit cell with density 3.2 g cm^{-3}. Edge length of the unit cell is 437 picometre (pm).

23. The type of unit cell is

(A) simple cubic (B) bcc

(C) fcc (D) edge-centered

24. The nearest neighbor distance is

(A) 154.5 pm (B) 309 pm

(C) 218.5 pm (D) 260 pm

25. The number of nearest neighbors of a Ca atom is

(A) 4 (B) 6

(C) 8 (D) 12

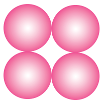
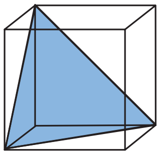
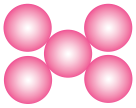
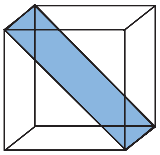
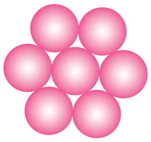
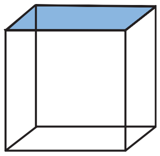
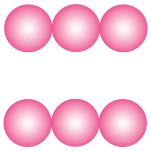
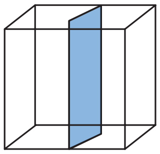
26. When the metal is melted, the density of the molten metal is found to be 3 g cm^{-3}. What will be the percentage of empty space in the melt?

(A) 31% (B) 36%

(C) 28% (D) 49%

Matrix-Match Type

27. Match the arrangment of atoms/ions with their planes in fcc lattice.

Column I	Column II
(A) 	(p) 
(B) 	(q) 
(C) 	(r) 
(D) 	(s) 

28. Match the edge length of a cube with its characteristics distance between atoms/ions in different compounds.

Column I	Column II
(A) $0.866\,a$	(p) Shortest distance between cation and anion in CsCl structure
(B) $0.707\,a$	(q) Shortest distance between two cations in CaF_2 structure
(C) $0.433\,a$	(r) Shortest distance between carbon atoms in diamond
	(s) Shortest distance between two cations in rock salt structure

29.

Column I	Column II
(A) Spinel structure	(p) $ZnAl_2O_4$
(B) Glass	(q) Pseudo solid
(C) 6 : 6 Co-ordination	(r) NaCl type structure
(D) Plastics	(s) Super cooled liquid

ATOMIC STRUCTURE

Single Correct Choice Type

1. Number of α-particles scattered by an angle θ in Rutherford's experiment is

(A) directly proportional to $(\text{K.E.})^2$.

(B) directly proportional to Z^4.

(C) inversely proportional to e^4.

(D) inversely proportional to $(\text{K.E.})^2$.

2. Light of wavelength λ shines on a metal surface with intensity x and the metal emits y electrons per second of average energy, z. What will happen to y and z if x is doubled?

(A) y will be doubled and z will become half.

(B) y will remain the same and z will be doubled.

(C) both y and z will be doubled.

(D) y will be doubled but z will remain the same.

3. How many electrons can fit into the orbitals that comprise the third quantum shell $n = 3$?

(A) 2 (B) 8

(C) 18 (D) 32

4. Which one of the following represents an impossible arrangement?

	n	l	m	s
(A)	3	2	–2	1/2
(B)	4	0	0	1/2
(C)	3	2	–3	1/2
(D)	5	3	0	1/2

5. The nucleus of an atom is located at $x = y = z = 0$. If the probability of finding an s-orbital electron in a tiny volume around $x = a, y = z = 0$ is 1×10^{-5}, what is the probability of finding the electron in the same sized volume around $x = z = 0, y = a$?

(A) 1×10^{-5} (B) $1 \times 10^{-5} \times a$

(C) $1 \times 10^{-5} \times a^2$ (D) $1 \times 10^{-5} \times a^{-1}$

6. If n and l are respectively the principal and azimuthal quantum numbers, then the expression for calculating the total number of electrons in any energy level is

(A) $\sum_{l=0}^{l=n} 2(2l+1)$ (B) $\sum_{l=1}^{l=n-1} 2(2l+1)$

(C) $\sum_{l=0}^{l=n+1} 2(2l+1)$ (D) $\sum_{l=0}^{l=n-1} 2(2l+1)$

7. A photon was absorbed by a hydrogen atom in its ground state and the electron was promoted to the fifth orbit. When the excited atom returned to its ground state, visible quanta were emitted when electron made the transition

(A) $5 \rightarrow 2$ (B) $2 \rightarrow 1$

(C) $3 \rightarrow 1$ (D) $4 \rightarrow 1$

8. In center-symmetrical system, the orbital angular momentum, a measure of the momentum of a particle travelling around the nucleus, is quantized. Its magnitude is

(A) $\sqrt{l(l+1)}\,\dfrac{h}{2\pi}$ (B) $\sqrt{l(l-1)}\,\dfrac{h}{2\pi}$

(C) $\sqrt{s(s+1)}\,\dfrac{h}{2\pi}$ (D) $\sqrt{s(s-1)}\,\dfrac{h}{2\pi}$

9. An electron, a proton and an alpha particle have kinetic energies of 16 E, 4 E and E respectively. What is the qualitative order of their de-Broglie wavelengths?

(A) $\lambda_e > \lambda_p = \lambda_\alpha$
(B) $\lambda_p = \lambda_\alpha > \lambda_e$
(C) $\lambda_p > \lambda_e > \lambda_\alpha$
(D) $\lambda_\alpha < \lambda_e \gg \lambda_p$

10. The dissociation energy of H_2 is 430.53 kJ mol^{-1}. If H_2 is dissociated by illuminating with the radiation of wavelength 253.7 nm, the fraction of the radiant energy which will be converted into kinetic energy is given by

(A) 8.76%
(B) 12.33%
(C) 11.3%
(D) 100%

11. The radii of two of the first four Bohr orbits of the hydrogen atom are in the ratio 1 : 4. The energy difference between them may be

(A) either 12.09 eV or 3.4 eV.
(B) either 2.55 eV or 10.2 eV.
(C) either 13.6 eV or 3.4 eV.
(D) either 3.4 eV or 0.85 eV.

12. The Z-component of angular momentum of an electron in an atomic orbital is governed by the

(A) principal quantum number.
(B) azimuthal quantum number.
(C) magnetic quantum number.
(D) spin quantum number.

13. In an atomic orbital the sign of the lobes indicates the

(A) sign of the probability distribution.
(B) sign of charge.
(C) sign of wave function.
(D) presence or absence of electron.

14. Radius of third orbit of Li^{2+} ion is x cm then de-Broglie's wavelength of electrons in the first orbit is

(A) $\dfrac{2\pi x}{3}$ cm
(B) $6\pi x$ cm
(C) $3\pi x$ cm
(D) $\dfrac{2\pi x}{6}$ cm

15. A proton accelerated from rest through a potential difference of V volts has a wavelength λ associated with it. An alpha particle in order to have the same wavelength must be accelerated from rest through a potential difference of

(A) V volt
(B) $4V$ volt
(C) $2V$ volt
(D) $\dfrac{V}{8}$ volt

Multiple Correct Choice Type

16. The wave functions of 3s and 3p_z orbitals are given by

$$\psi_{3s} = \frac{1}{9\sqrt{3}}\left(\frac{1}{4\pi}\right)^{\frac{1}{2}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}\left(6-\frac{4Zr}{a_0}+\frac{4}{9}\frac{Z^2r^2}{a_0^2}\right)e^{\frac{-Zr}{3a_0}}$$

$$\frac{1}{9\sqrt{6}}\left(\frac{3}{4\pi}\right)^{\frac{1}{2}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}\left(4-\frac{2Zr}{3a_0}\right)\left(\frac{2Zr}{3a_0}\right)e^{-\frac{Zr}{3a_0}}\cos\theta$$

From these we can conclude that

(A) the number of nodal surfaces for 3p_z and 3s orbitals are equal.
(B) the angular nodal surface of 3p_z orbital has the equation $\theta = \dfrac{\pi}{2}$.
(C) the radial nodal surfaces of 3s orbital and 3p_z orbitals are at equal distance from the nodes.
(D) 3s electrons have greater penetrating power into the nucleus in comparison to 3p electrons.

17. In a hydrogen-like sample electron is in the second excited state, and the binding energy of fourth state of this sample is 13.6 eV. Then

(A) 25 eV photon can set free the electron from the second excited state of this sample.
(B) three different types of photons will be observed if electrons make transition to the ground state from the second excited state.
(C) if 23 eV photon is used, then, K.E. of the ejected electron is 1 eV.
(D) second line of Balmer series of this sample has the same energy value as first excitation energy of hydrogen atoms.

18. First excitation potential for the hydrogen-like (hypothetical) sample is 24 V. Then

(A) ionization energy of the sample is 36 eV.
(B) ionization energy of the sample is 32 eV.

(C) binding energy of third excited state is 2 eV.

(D) second excitation potential of the sample is $\dfrac{32\times 8}{9}$ V.

19. A hydrogen-like atom in the ground state absorbs '*n*' photons having the same energy and it emits exactly '*n*' photons when electronic transition takes place. Then the energy of the absorbed photon may be

(A) 91.8 eV (B) 40.8 eV
(C) 48.4 eV (D) 54.4 eV

20. Hydrogen atoms are in a particular excited state '*n*'. When all these returned to ground state, 6 different photons are emitted. Which of the following is/are incorrect?

(A) Out of the six different photons, only two photons have speed equal to that of visible light.

(B) If highest energy photon emitted from the above sample is incident on the metal plate having work function 8 eV, K.E. of liberated photoelectron may be equal to or less than 4.75 eV.

(C) Total number of radial nodes in all the orbitals of n^{th} shell is 24.

(D) Total number of angular nodes in all the orbitals in $(n–1)^{\text{th}}$ shell is 23.

Assertion-Reasoning Type

Choose the correct option from the following:

(A) Statement 1 and Statement 2 are True, Statement 2 is the correct explanation of the Statement 1.

(B) Statement 1 and Statement 2 are True, Statement 2 is NOT a correct explanation of the Statement 1.

(C) Statement 1 is True, Statement 2 is False.

(D) Statement 1 is False, Statement 2 is True.

21. Statement 1: The charge to mass ratio of the particles in anode rays depends on nature of the gas taken in the discharge tube.

Statement 2: The particles in anode rays carry positive charge.

22. Statement 1: *s* orbital cannot accommodate more than two electrons.

Statement 2: *s* orbitals are spherically symmetrical.

23. Statement 1: Kinetic energy of photoelectrons is directly proportional to the intensity of the incident radiation.

Statement 2: Each photon of light causes the emission of only one photo electron.

24. Statement 1: The existence of three unpaired electrons in phosphorous atom can be explained on the basis of Hund's rule.

Statement 2: According to Hund's rule, the degenerate orbitals are first singly occupied and only then pairing takes place.

25. Statement 1: If an electron is located within the range of 0.2 Å then the uncertainty in velocity is approximately 6×20^{6} m s^{-1}.

Statement 2: Trajectory (path of motion) of above electron can be defined ($h = 6.6 \times 20^{-34}$, $m_e = 9.2\times 20^{-31}$ kg)

Comprehension Type

Paragraph I

Assume that there were four possible values $(-1, \frac{1}{2}, +\frac{1}{2}, +1)$ for the spin quantum number m_s. Principal quantum number *n* is defined as usual. However, quantum numbers *l* and m_l are defined as follows:
l: 1 to $(n+1)$ in integral steps
$m_{l^3}: -\frac{1}{2}$ to $+\frac{1}{2}$ (including zero, if any) in integral steps.
The orbitals corresponding to l = 1, 2, 3… are designated as A, B, C,... respectively. Further, the values of m_l for a given value of *l* give the number of sub-orbitals in an orbital.
The principles for filling electrons in the shells remain unchanged. The order of energies of various orbitals is: A < B < C… for the same shell.

26. The number of elements that would be present in the second period of the periodic table is

(A) 9 (B) 20
(C) 24 (D) 36

27. The second period would begin with

(A) fluorine
(B) sodium
(C) calcium
(D) scandium

28. The number of sub-orbitals and the maximum number of electrons that can be filled in Eorbitals are, respectively

(A) 6, 24 (B) 5, 20

(C) 7, 28 (D) cannot be determined

Paragraph II

Orbital wave function ψ can be written as

$$\psi(r,\theta,\phi) = R(r)\cdot\Theta(\theta)\cdot\Phi(\phi)$$

For various orbitals of hydrogen atom and hydrogen like atoms, values of R (radial wave function) are

For 1*s* orbital: $R_{1s} = \left(\dfrac{Z}{a_0}\right)^{\frac{3}{2}} e^{\frac{-Zr}{a_0}}$

For 2*s* orbital: $R_{2s} = \left(\dfrac{Z}{2a_0}\right)^{\frac{3}{2}}\left(2-\dfrac{Zr}{a_0}\right)e^{\frac{-Zr}{2a_0}}$

For 1*p* orbital: $R_{2p} = \dfrac{1}{\sqrt{3}}\left(\dfrac{Z}{2a_0}\right)^{\frac{3}{2}}\left(\dfrac{Zr}{a_0}\right)\times e^{\frac{-Zr}{2a_0}}$

For 3*s* orbital:

$$R_{3s} = \frac{2}{3}\left(\frac{Z}{3a_0}\right)^{\frac{3}{2}}\left(3-\frac{2Zr}{a_0}+\frac{2Z^2r^2}{9a_0^2}\right)\times e^{\frac{-Zr}{3a_0}} \text{ and so on.}$$

Here $a_0 = \text{Bohr radius} = \dfrac{4\pi \in_0 \hbar^2}{\mu e^2}$

Similarly angular functions Θ and Φ can also be given as follows for *s* orbital.

$$\Theta(\theta) = \frac{1}{\sqrt{2}} \text{ and } \Phi(\phi) = \frac{1}{\sqrt{2\pi}}$$

So for 1*s* orbital ψ can be given as

$$\psi_{1s} = R_{1s}\cdot\Theta_{1s}\cdot\Phi_{1s}$$

$$= \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{\frac{-Zr}{a_0}}$$

29. Probability density of finding an electron at distance r from nucleus in hydrogen atom (in ground state) is

(A) ψ (B) R^2

(C) $\dfrac{1}{\pi}\left(\dfrac{Z}{a_0}\right)^3 e^{\frac{-2Zr}{a_0}}$ (D) None of these

30. Value of r at which radial node is found for 2*s* orbital is

(A) a_0 (B) $2a_0$

(C) $3a_0$ (D) $4a_0$

31. Radial nodes for 3*s* orbital is/are at

(A) $r = 1.9\ a_0$ (B) $r = 7.1\ a_0$

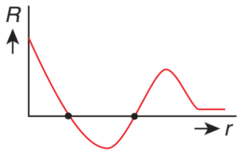
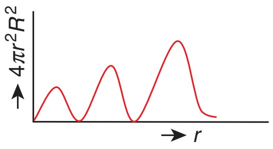
(C) $r = 2\ a_0$ (D) Both (A) and (B)

Matrix-Match Type

32. Match the orbitals and their characteristics.

Column I	Column II
(A) Orbitals having equal energy	(p) 3*p*, 3*d*
(B) Orbitals having zero orbital angular momentum	(q) 2*s* and 3*s*
(C) Orbitals with only one spherical node	(r) Degenerate orbitals
(D) Orbitals having directional character	(s) 2*s* and 3*p*

33. Match the orbitals and their characteristics.

Column I	Column II
(A) 	(p) $3p_z$
(B) 	(q) $4p_y$
(C) Angular probability is dependent on θ and ϕ	(r) 3*s*
(D) At least one angular node is present	(s) $3p_x$

CHEMICAL BONDING

Single Correct Choice Type

1. The molecule BF_3 and NF_3 both are covalent compounds. But BF_3 is non-polar and NF_3 is polar. The reason is that

(A) boron is a metal and nitrogen is a gas in uncombined state.

(B) BF_3 bonds have no dipole moment whereas NF_3 bonds have dipole moment.

(C) atomic size of boron is smaller than that of nitrogen.

(D) BF_3 is symmetrical molecule where as NF_3 is unsymmetrical.

2. Example of $p\pi - p\pi$ bonding is

(A) BF_3 (B) SO_2

(C) SO_3 (D) All of these

3. The hybridization state of B in B_2H_6 is

(A) sp (B) sp^2

(C) sp^3 (D) sp^3d

4. The observed dipole-moment of HCl molecule is 1.03 D. If H—Cl bond distance is 1.275 Å and electronic charge is 4.8×10^{-10} esu, what is the percent polarity of HCl?

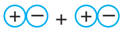
(A) $1.275\ \text{Å} \times 1.03$

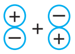
(B) $\dfrac{4.8\times10^{-10}\times1.275\times10^{-8}}{1.03}$

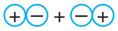
(C) $\dfrac{1.03\times100\times10^{-18}}{4.8\times10^{-10}\times1.275\times10^{-8}}$

(D) $\dfrac{4.8\times10^{-10}}{1.03}\times10$

5. Effective overlapping will be shown by

(A) 

(B) 

(C) 

(D) All the above

6. The structure of Br_3^- involves hybridization of the type

(A) sp^3d (B) sp^3d^2

(C) dsp^3 (D) d^2sp^3

7. Which of the following statement is/are not correct?

(A) CH_3^+ shows sp^2 hybridization whereas CH_3^- shows sp^3 hybridization.

(B) NH_4^+ has a regular tetrahedral geometry.

(C) sp^2 hybridized orbitals have equal s and p character.

(D) Hybridized orbitals always form σ bonds.

8. Match the items under List I with the items under List II and select the correct answer using the codes given below the lists

List I (Hybridization)	List II (Shape)
(a) dsp^2	(1) Square planar
(b) sp^3	(2) Tetrahedral
(c) d^2sp^3	(3) Octahedral
(d) sp^3d	(4) Trigonal bipyramidal

(A) (a) → 1; (b) → 2; (c) → 3; (d) → 4

(B) (a) → 4; (b) → 2; (c) → 3; (d) → 1

(C) (a) → 1; (b) → 3; (c) → 2; (d) → 4

(D) (a) → 1; (b) → 4; (c) → 3; (d) → 3

9. In the 8.4 g N_2, total number of π electrons would be

(A) $1.2\ N_A$ (B) $1.8\ N_A$

(C) $2.4\ N_A$ (D) $0.6\ N_A$

10. The correct order of the O–O bond length in O_2, H_2O_2 and O_3 is

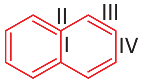
(A) $O_3 > H_2O_2 > O_2$

(B) $O_2 > H_2O_2 > O_3$

(C) $O_2 > O_3 > H_2O_2$

(D) $H_2O_2 > O_3 > O_2$

11. Naphthalene has four different types of carbon-carbon bonds as shown by the following figure.



The shortest carbon-carbon bond is

(A) I (B) II

(C) III (D) IV

12. Which of the following molecular orbital has two nodal planes?

(A) $\sigma 2s$ (B) $\pi{*}2p_y$

(C) $\sigma 2p_z$ (D) $\sigma{*}2p_x$

13. In which excited state iodine shows sp^3d^3 hybridization state?

(A) Zero (B) First

(C) Second (D) Third

14. Which of the following has shape most near to pyramidal shape?

(A) $^\bullet CH_3$ (B) $^\bullet CH_2F$

(C) $^\bullet CHF_2$ (D) $^\bullet CF_3$

15. Correct order of bond angle is

(A) $PF_3 < PH_3$ (B) $PH_3 < PF_3$

(C) $PF_3 = PH_3$ (D) cannot be predicted.

16. How many covalent and how many coordinate bonds are present in Al_2Cl_6?

(A) 6, 2 (B) 7, 0

(C) 4, 4 (D) 8, 0

17. O–O bond length in H–O–O–H and F–O–O–F respectively are

(A) 1.22 Å, 1.48 Å (B) 1.48 Å, 1.22 Å

(C) 1.22 Å, 1.22 Å (D) 1.48 Å, 1.48 Å

18. Match the items under List I with items under List II and select the correct answer from the codes given below the lists

List I (Molecule)	List II (Shape)
(a) PCl_5	(p) V-shaped
(b) F_2O	(q) Triangular planar
(c) BCl_3	(r) Trigonal bipyramidal
(d) NH_3	(s) Trigonal pyramidal
	(t) Tetrahedral

(A) (a) → p, (b) → t, (c) → s, (d) → r

(B) (a) → q, (b) → r, (c) → p, (d) → q

(C) (a) → s, (b) → r, (c) → q, (d) → t

(D) (a) → r, (b) → p, (c) → q, (d) → s

19. The bond angles of NH_3, NH_4^+ and NH_2^- are in the order

(A) $NH_2^- > NH_3 > NH_4^+$

(B) $NH_4^+ > NH_3 > NH_2^-$

(C) $NH_3 > NH_2^- > NH_4^+$

(D) $NH_3 > NH_4^+ > NH_2^-$

20. In an antibonding molecular orbital, electron density is minimum

(A) around one atom of the molecule.

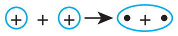
(B) between the two nuclei of the molecule.

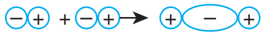
(C) at the region away from the nuclei of the molecule.

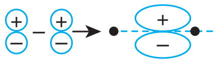
(D) at no place.

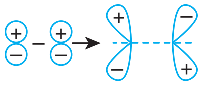
Multiple Correct Choice Type

21. Which of the following overlap of orbitals is/are incorrect?

(A) 

(B) 

(C) 

(D) 

22. The type of bonds present in PH_4I are

(A) ionic. (B) covalent.

(C) coordinate. (D) H–bonds.

23. What is correct about PCl_5 molecule?

(A) The molecule has pentagonal planar shape.

(B) It has two types of P–Cl bonds.

(C) All the P–Cl bonds are of equal length.

(D) The molecule has trigonal bipyramidal shape.

24. Which of the following statements are not correct?

(A) All C—O bonds in CO_3^{2-} are equal but not in H_2CO_3.

(B) All C—O bond in HCO_2^- are equal but not in HCO_2H.

(C) C—O bond length in HCO_2^- is longer than C—O bond length in CO_3^{2-}.

(D) C—O bond length in HCO_2^- and C—O bond length in CO_3^{2-} are equal.

25. In the structure of H_2CSF_4, which of the following statement is/are correct?

(A) Two C—H bonds are in the same plane of axial S—F bonds.

(B) Two C—H bonds are in the same plane of equatorial S—F bonds.

(C) Total six atoms are in the same plane.

(D) Equatorial S—F plane is perpendicular to the nodal plane of π bond.

Assertion-Reasoning Type

Choose the correct option from the following:

(A) Statement 1 and Statement 2 are True, Statement 2 is the correct explanation of the Statement 1.

(B) Statement 1 and Statement 2 are True, Statement 2 is NOT a correct explanation of the Statement 1.

(C) Statement 1 is True, Statement 2 is False.

(D) Statement 1 is False, Statement 2 is True.

26. **Statement 1:** XeF_2 is a linear molecule.
Statement 2: Xe atom assumes *sp* hybrid state in XeF_2.

27. **Statement 1:** The bond angle of directed bonds around S in H_2S is 92º.
Statement 2: S atom in H_2S is sp^3 hybridized.

28. **Statement 1:** O_2 molecule is paramagnetic in nature.
Statement 2: O_2 molecule contains two unpaired electrons in antibonding orbitals.

29. **Statement 1:** First group elements are very good reducing agents.
Statement 2: First group elements have low sublimation energy and low ionization energy hence these elements have very high negative standard reduction potential.

Comprehension Type

Paragraph I

The potential energy *W* of a system of two atoms A and B varies as a function of their distance of separation *r* as follows:

$$W = -\frac{A'}{r^n} + \frac{B'}{r^m}$$

where A′ and B′ are characteristic constants independent of *r*.

30. The bond distance between A and B that is d_{A-B} is given by

(A) $d_{A-B} = \left(\frac{mB'}{nA'}\right)^{\frac{1}{m-n}}$

(B) $d_{A-B} = \left(\frac{nA'}{mB'}\right)^{\frac{1}{m-n}}$

(C) $d_{A-B} = \frac{mB'}{nA'}$

(D) $d_{A-B} = \left(\frac{mB'}{nA'}\right)^{\frac{m}{n}}$

31. The bond dissociation energy of A–B bond, D_{A-B}, is given by:

(A) $D_{A-B} = \frac{A'}{r^n}\left(1 - \frac{n}{m}\right)$

(B) $D_{A-B} = \frac{A'}{r^m}\left(1 - \frac{n}{m}\right)$

(C) $D_{A-B} = \frac{A'}{r^n}\left(\frac{m}{n} - 1\right)$

(D) $D_{A-B} = \frac{n}{m}$

32. In diamond each C atoms are sp^3 hybridized and each C atom is attached with four other C atoms. The C–C single bond energy is 350 kJ mol^{-1}. Therefore enthalpy of atomization of diamond is

(A) 700 kJ mol^{-1} (B) 350 kJ mol^{-1}

(C) 175 kJ mol^{-1} (D) 1050 kJ mol^{-1}

33. When there is no bond between atoms of element A and B (when atoms of A and B are at ∞ distance), then the potential energy is conside red

(A) minimum. (B) zero.

(C) non-zero. (D) cannot be predicted.

Paragraph II

You are given four cations, A^+, B^{2+}, C^{3+} and D^{3+}. The radius of the cations is as follows

Cation	Radius (Å)
A^+	0.6
B^{2+}	1.20
C^{3+}	0.50
D^{3+}	0.80

34. Basic oxide among the following is

(A) A_2O (B) BO

(C) D_2O_3 (D) All of these

35. Amphoteric oxide among the following is

(A) A_2O (B) BO

(C) C_2O_3 (D) P_2O_3

36. Which of the following ion has maximum value of ionic potential (ϕ)?

(A) A^+ (B) B^{2+}

(C) C^{3+} (D) D^{3+}

Matrix-Match Type

37. Match the compound with the type of bond.

Column I	Column II
(A) NH_4Cl	(p) Hydrogen bond
(B) $CuSO_4 \cdot 5H_2O$	(q) Co-ordinate bond
(C) HNC	(r) Ionic bond
(D) Liquid H_2O_2	(s) Covalent bond

38. Match the pair of species with their identical properties.

Column I	Column II
(A) PCl_3F_2 and PCl_2F_3	(p) Hybridization of central atom
(B) BF_3 and BCl_3	(q) Shape of molecule/ion
	(r) μ (dipole moment)
(C) CO_2 and CN_2^{-2}	
(D) C_6H_6 and $B_3N_3H_6$	(s) Total number of electrons

CHEMICAL ENERGETICS

Single Correct Choice Type

1. An ideal gas is filled in compartment A of a container as shown below.

A	B
5 mol 5 L	5 L

Compartment B is empty and volume of both A and B is 5 L each. Partition between A and B compartments are removed suddenly. If pressure of gas in A was initially 4 atm then work done by gas during expansion is (Assuming no heat exchange with surroundings.)

(A) 10 atm L (B) 40 atm L

(C) 0 (D) 20 atm L

2. A perfect gas undergoes a reversible adiabatic expansion from 27°C, 200 atm to −183°C and 10.00 atm. The probable molecularity of the gas is $\left(\text{Given } \ln\dfrac{10}{3} = 1.2 \text{ and } \ln 20 = 2.99\right)$

(A) 1 (B) 2

(C) 3 (D) 4

3. Lattice enthalpy of NaCl is {Given: $\Delta_f H^\circ$ (NaCl) = −410.87 kJ mol^{-1}; Ionization enthalpy of Na = 495.8 kJ mol^{-1}; Electron gain enthalpy of Cl = 365.26 kJ mol^{-1}; $\Delta_{sub}H$ of Na = 317.57 kJ mol^{-1}; $\Delta_{bond}H$ of $Cl_2(g)$ = 241.84 kJ mol^{-1}}

(A) 979.9 kJ mol^{-1} (B) 97.99 kJ mol^{-1}

(C) 9.799 kJ mol^{-1} (D) 9799 kJ mol^{-1}

4. A 0.138 g sample of Mg (molar mass = 24.3 g mol^{-1}) is burnt in a constant volume bomb calorimeter that has a heat capacity of 1.77 kJ °C^{-1}. Calorimeter contains 300 mL of water (density 1 g mL^{-1}) and its temperature is raised by 1.126°C. Enthalpy of combustion of Mg is

(A) – 599.60 kJ mol^{-1} (B) 599.60 kJ mol^{-1}

(C) – 350.94 kJ mol^{-1} (D) 350.94 kJ mol^{-1}

5. Given:

$HCl(g) + 40\,H_2O(l) \rightarrow HCl(40\,H_2O)$;
$\Delta_r H = -73$ kJ mol^{-1}
$HCl(g) + 200\,H_2O(l) \rightarrow HCl(200\,H_2O)$;
$\Delta_r H = -74$ kJ mol^{-1}

From the above data integral enthalpy of dilution of $HCl(40\,H_2O)$ into $HCl(200\,H_2O)$ is,

(A) −74 kJ mol^{-1} (B) −73 kJ mol^{-1}

(C) −1 kJ mol^{-1} (D) +1 kJ mol^{-1}

6. An engine operates in a Carnot cycle and absorbs 3 kJ heat at 400 K. If the engine evolves some heat at 300 K in each cycle, then work done by engine in one cycle is

(A) −0.75 kJ (B) 5.25 kJ

(C) +0.75 kJ (D) −5.25 kJ

7. ΔS for 3 moles of a diatomic ideal gas which is heated and compressed from 298 K and 1 bar to 398 K and 5 bar is

$\left(\text{Given: } C_{p,m} = \dfrac{7}{2}R; \ln\dfrac{398}{298} = 0.29; \ln 5 = 1.61\right)$

(A) −14.84 J K^{-1} (B) +14.84 J K^{-1}

(C) −4.97 J K^{-1} (D) +4.97 J K^{-1}

8. Which among the following do not have zero entropy at absolute zero temperature (0 K)?

(A) CO (B) NO

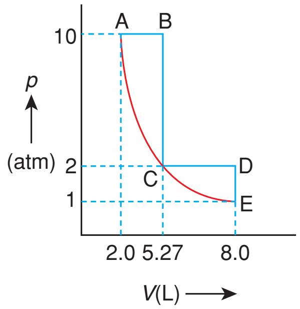
(C) H_2 (D) All

9. An ideal gas expands in an isothermal reversible process. Gas is filled in a cylinder fitted with a movable piston of 20 cm diameter. If initial and final volumes of gas are 1 L and 16 L, then find out the distance travelled by piston (in cm) when one-fourth of the work has been done during expansion.

(A) $5/\pi$ (B) $10/\pi$

(C) $\pi/5$ (D) 20

10. An ideal monoatomic gas undergoes a volume change as shown in the figure below.



Value of $\dfrac{w_{\text{ABCDE}}}{w_{\text{ACE}}}$ is

[Given: 5/3 log 2 = log 3.2 log 5.27 = log 16.] Give your answer in the form of nearest integer.

(A) 1
(B) 2
(C) 3
(D) 4

11. A solution of 500 mL of 0.2 M KOH and 500 mL of 0.2 M HCl is mixed and stirred; the rise in temperature is T_1. The experiment is repeated using 250 mL of each of the solution, the temperature raised is T_2. Which of the following is true?

(A) $T_1 = T_2$
(B) $T_1 = 2T_2$
(C) $T_1 = 4T_2$
(D) $T_2 = 9T_1$

12. For the reaction

$X_2O_4\ (l) \longrightarrow 2XO_2\ (g); \Delta E = 2.1$ kcal, $\Delta S = 20$ cal K^{-1} at 300 K. Hence ΔG is

(A) 2.7 kcal
(B) −2.7 kcal
(C) 9.3 kcal
(D) −9.3 kcal

13. Which of the following processes proceed towards more disordered state?

I. Stretching the rubber
II. Sublimation of dry ice
III. Crystallization of salt from its solution
IV. Dissolution of sugar

(A) I, II, IV
(B) I, III
(C) III, IV
(D) II, IV

14. The following reaction occurs at 25°C

$$2NO\ (g, 1 \times 10^{-5}\ \text{atm}) + Cl_2\ (g, 1 \times 10^{-2}\ \text{atm}) \rightleftharpoons 2NOCl\ (g, 1 \times 10^{-2}\ \text{atm})$$

ΔG^o for the reaction is

(A) −45.65 kJ
(B) −28.53 kJ
(C) −22.82 kJ
(D) −57.06 kJ

15. An ideal gas expands from volume V_1 to V_2. This may be achieved by any of the three processes: isobaric, isothermal and adiabatic. Let ΔU be the change in internal energy of the gas. w be the work done by the system on the gas. Identify which of the following statements is not true for ΔU?

(A) ΔU is the least in the adiabatic expansion.
(B) ΔU is the greatest in the adiabatic expansion.
(C) ΔU is the greatest under isobaric process.
(D) ΔU in isothermal process lies in-between the values obtained under isobaric and adiabatic process.

16. Which of the following statements is true regarding reversible adiabatic expansion of an ideal gas?

(A) Plot of T vs. V is a straight line with slope equal to γ.
(B) Plot of $\ln T$ vs. $\ln V$ is a straight line with slope equal to γ.
(C) Plot of $\ln T$ vs. $\ln V$ is a straight line with slope equal to $-\gamma$.
(D) Plot of $\ln T$ vs. $\ln V$ is a straight line with slope $(1-\gamma)$.

Multiple Correct Choice Type

17. In which of the following process, entropy increases?

(A) Rusting of iron.
(B) Vaporization of camphor.
(C) Crystallization of sugar from syrup.
(D) Atomization of dihydrogen.

18. Which of the following statements is/are correct?

(A) Absolute value of internal energy cannot be determined.
(B) Absolute value of heat content can be determined.
(C) Absolute value of entropy can be determined.
(D) All the three U, H and S are extensive properties.

19. The criteria for spontaneity of a process is/are

(A) $(dG)_{T,p} < 0$
(B) $(dU)_{S,V} < 0$
(C) $(dH)_{S,p} < 0$
(D) $(dS)_{U,V} < 0$

20. Substances which have zero $\Delta_f H^o$ is/are

(A) C (s, graphite)
(B) C (s, diamond)
(C) P_4 (s, white)
(D) Br_2 (gas)

21. Two moles of a monoatomic ideal gas ($C_V = 1.5R$) initially at 400 K in an isolated, 1.0 L, container with piston is allowed to expand against a constant pressure of a 1.0 atm till the final volume reaches to 10 L. Which of the following conclusions regarding the above changes(s) is (are) true?

(A) The final temperature of the gas is 363 K (approx).

(B) If the same process were carried out to the same final volume but under reversible conditions, final temperature would have been less than 363 K.

(C) In the above process, the initial and final temperatures and volumes are related as $\left(\frac{T_1}{T_2}\right) = \left(\frac{V_2}{V_1}\right)^{\gamma-1}$.

(D) Entropy change of a system (ΔS_{system}) is zero.

22. Which of the following thermodynamic relation(s) is (are) correct?

(A) In a cyclic process, $\oint dS = 0$ (at constant p)

(B) $\Delta G = -T\Delta S_{\text{univ}}$

(C) $\left(\frac{\partial G}{\partial T}\right)_p = -S$

(D) $\Delta G = \Delta G^\circ + RT \ln Q$

23. According to second law of thermodynamics

(A) heat cannot flow spontaneously from a reservoir at lower temperature to a reservoir at higher temperature.

(B) all spontaneous processes lead to increase in entropy of the universe.

(C) melting of a solid increases entropy, therefore it is a spontaneous process.

(D) processes in which $\Delta S_{\text{sys}} > 0$ are spontaneous.

Assertion-Reasoning Type

Choose the correct option from the following:

(A) Statement 1 and Statement 2 are True, Statement 2 is the correct explanation of the Statement 1.

(B) Statement 1 and Statement 2 are True, Statement 2 is NOT a correct explanation of the Statement 1.

(C) Statement 1 is True, Statement 2 is False.

(D) Statement 1 is False, Statement 2 is True.

24. **Statement 1:** A precipitation reaction always decreases randomness, hence decreases entropy of the system and therefore is non-spontaneous.
Statement 2: Spontaneity is related to entropy change of universe.

25. **Statement 1:** Chemical equation,
$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l); \Delta H = -x$ kJ
represents enthalpy of formation of water.
Statement 2: $\Delta H_{\text{neutralization}}$ of strong acid-strong base is never constant.

26. **Statement 1:** No heat engine has an efficiency of 100%.
Statement 2: Complete conversion of heat into work is not possible.

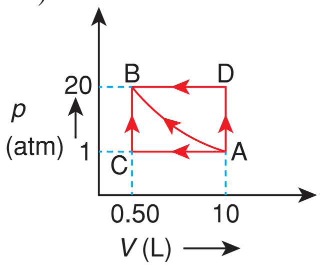
27. **Statement 1:** $\Delta_f G^\circ(\text{graphite}) = 0$

Statement 2: For free elements in their standard state, $\Delta_f G^\circ$ may not be taken as zero.

Comprehension Type

Paragraph I

Assume perfect gas behavior in the following isotherm ($T = 313$).



28. Number of moles of gas in this system at the start is

(A) 0.39 (B) 0.17
(C) 0.78 (D) 0.34

29. Work done on the gas along the path DAC is

(A) 0.96 kJ (B) +3.0 kJ
(C) –5.0 kJ (D) +7.1 kJ

30. ΔU for path ACB is

(A) 19.7 kJ (B) zero
(C) 51.2 kJ (D) 3.0 kJ

Paragraph II

The second law of thermodynamics is a fundamental law of science. In this problem, we consider the thermodynamics of an ideal gas, phase transition and chemical equilibrium.

Five moles of CO_2 gas expand isothermally (in thermal contact with surrounding temperature

= 15ºC) against a fixed external pressure of 1.00 bar. The initial and final volume of gas is 10.0 L and 30.0 L respectively.

31. Assuming CO_2 to be an ideal gas, ΔS_{sys} is

(A) 27.4 J K^{-1} mol^{-1} (B) 9.1 J K^{-1} mol^{-1}

(C) –27.4 J K^{-1} mol^{-1} (D) –9.15 J K^{-1} mol^{-1}

32. If the expansion of gas takes place reversibly then ΔS_{sys} would have been

(A) 19.82 J K^{-1} (B) 45.66 J K^{-1}

(C) 84.21 J K^{-1} (D) 9.1 J K^{-1}

33. ΔS_{surr} is

(A) –27.4 J K^{-1} (B) 6.94 J K^{-1}

(C) 0.00 J K^{-1} (D) –6.94 J K^{-1}

Matrix-Match Type

34. Match the process with the change in thermodynamic quantity.

Column I	Column II
(A) Melting of solids at normal melting points	(p) $\Delta S_{univ} = 0$
(B) Effusing of a gas from gas cylinder	(q) $\Delta G = 0$
(C) Freezing of water at 0ºC and 1.0 atm	(r) $\Delta S_{sys} > 0$
(D) Vaporization of H_2O at 373 K and 0.90 atm	(s) $\Delta S_{surr} < 0$

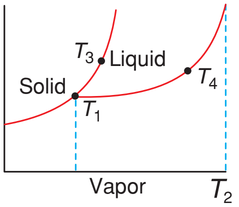
35. Match the thermodynamic quantity with its expression.

Column I	Column II
(A) dU	(p) $C_V \dfrac{dT}{T} + R\dfrac{dV}{V}$
(B) dH	(q) $V\mathrm{d}p + S\mathrm{d}T$
(C) dS (1 mol)	(r) $\mathrm{d}q + V\mathrm{d}p$
(D) dG	(s) $\mathrm{d}p - p\mathrm{d}V$

SOLUTIONS

Single Correct Choice Type

1. Observe the given pT phase diagram for a given substance A. Then melting point of A(s), boiling point of A(l), critical point of A and triple point of A (at their respective pressures) are respectively



(A) T_1, T_2, T_3, T_4 (B) T_4, T_3, T_1, T_2

(C) T_3, T_4, T_2, T_1 (D) T_2, T_1, T_3, T_4

2. The solubility of N_2(g) in water exposed to the atmosphere, when the partial pressure is 593 mm, is 5.3×10^{-4} M. Its solubility at 760 mm and at the same temperature is

(A) 4.1×10^{-4} M (B) 6.8×10^{-4} M

(C) 1500 M (D) 2400 M

3. The plot of $1/x_A$ versus $1/y_A$ (where x_A and y_A are the mole fractions of A in liquid and vapor phases respectively) is linear whose slope and intercept respectively are given as

(A) p_A^o/p_B^o, $(p_A^o - p_B^o)/p_B^o$

(B) p_A^o/p_B^o, $(p_B^o - p_A^o)/p_B^o$

(C) p_B^o/p_A^o, $(p_A^o - p_B^o)/p_B^o$

(D) p_B^o/p_A^o, $(p_B^o - p_A^o)/p_B^o$

4. At 323 K, the vapor pressure in mm of Hg of a methanol-ethanol solution is represented by the equation

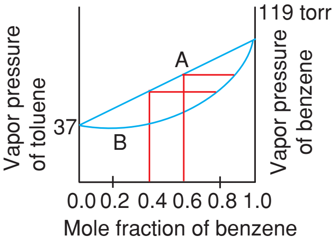
$$p = 120x_A + 140$$

where x_A is the mole fraction of methanol. Then the value of $\lim\limits_{x_A \to 1} \dfrac{p_A}{x_A}$ is

(A) 120 mm (B) 140 mm

(C) 260 mm (D) 20 mm

5. Choose the correct option.



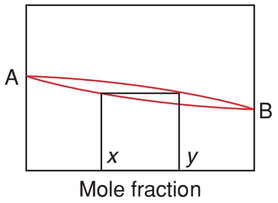
(A) A represents vapor composition and B liquid composition.

(B) A as well as B represent liquid composition.

(C) Both A and B represent vapor composition.

(D) A represents liquid composition and B vapor composition.

6. Consider the following graph. Which of the following statements is correct?



(A) A liquid mixture of composition x is in equilibrium with a vapor mixture of composition y.
(B) A liquid mixture of composition y is in equilibrium with a vapor mixture of composition x.
(C) $x = y^2$
(D) $y = x^2$

7. Water and chlorobenzene are immiscible liquids. Their mixture boils at 90°C under a reduced pressure of 9.58×10^4 Pa. The vapor pressure of pure water at 90°C is 7.03×10^4 Pa and molecular weight of chlorobenzene is 112.5. On what percent basis, chlorobenzene in the distillate is equal to

(A) 50 (B) 60
(C) 70 (D) 80

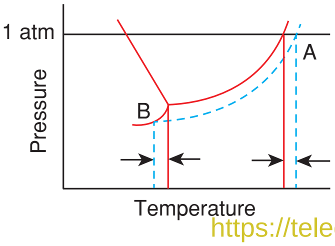
8. Vapor pressure of C_6H_6 and C_7H_8 mixture at 50°C is given by p (mm Hg) $= 180\, x_B + 90$, where x_B is the mole fraction of C_6H_6. A solution is prepared by mixing 936 g benzene and 736 g toluene and if vapors over this solution are removed and condensed into liquid and again brought to the temperature 50°C, what would be mole fraction of C_6H_6 in the vapor state. (At. wt. of C = 12, H = 1).

(A) $y'_B = 0.932$ (B) $y'_B = 0.72$
(C) $y'_B = 0.37$ (D) $y'_B = 0.42$

9. Calculate the ebullioscopic constant for water. The heat of vaporization is 40.685 kJ mol^{-1}.

(A) 0.512 K kg mol^{-1} (B) 1.86 K kg mol^{-1}
(C) 5.12 K kg mol^{-1} (D) 3.56 K kg mol^{-1}

10. The phase diagrams for a pure solvent (represented by the solid line) and a corresponding solution (containing a nonvolatile solute and represented by the dashed lines) are shown below.



Choose the correct option among the following.

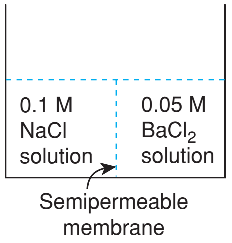
(A) $A = \Delta T_b m$ and $B = \Delta T_f m$
(B) $A = \Delta T_f m$ and $B = \Delta T_b m$
(C) $A = \Delta T_f$ and $B = \Delta T_b$
(D) $A = \Delta T_b$ and $B = \Delta T_f$

where T_f, T_b and m stand for freezing point temperature, boiling point temperature and molality.

11. Solute A is a ternary electrolyte and solute B is a non-electrolyte. If 0.1 M solution of solute B produces an osmotic pressure of $2p$, then 0.05 M solution of A at the same temperature will produce an osmotic pressure equal to

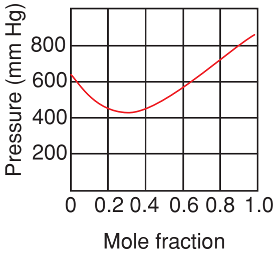
(A) $1.5p$ (B) $2p$
(C) $3p$ (D) p

12. Study the following figure, and choose the correct option.

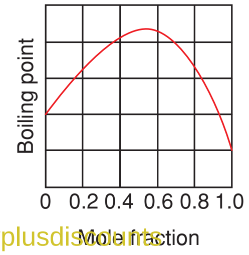


(A) There will be no movement of any solution across the membrane.
(B) Solvent of $BaCl_2$ will flow towards the NaCl solution.
(C) NaCl will flow towards the $BaCl_2$ solution.
(D) The osmotic pressure of 0.1 M NaCl is higher than the osmotic pressure of 0.05 M $BaCl_2$, assuming complete dissociation of the electrolyte.

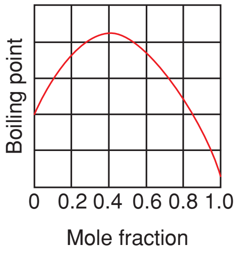
13. Given below is the p vs. x curve for a non-ideal liquid mixture. Identify the correct T vs. x curve for the same mixture.



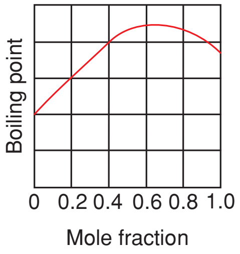
(A)



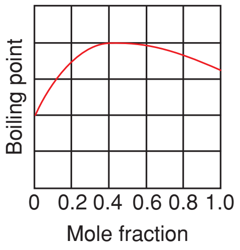
(B)



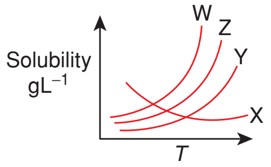
(C)



(D)



14. Solubility curves of four ionic salts X, Y, Z, W are given below.



In which case the value of $\Delta_{sol}H < 0$?

(A) X
(B) Y
(C) Z
(D) W

15. Three solutions are prepared by adding w g of A into 1 kg of water, w g of B into another 1 kg of water and w g of C in another 1 kg of water (A, B, C are non-electrolytic). Dry air is passed from these solutions in sequence (A → B → C). The loss in weight of solution A was found to be 2 g while solution B gained 0.5 g and solution C lost 1 g. Then the relation between molar masses of A, B and C is

(A) $M_A : M_B : M_C = 4 : 3 : 5$
(B) $M_A : M_B : M_C = \frac{1}{4} : \frac{1}{3} : \frac{1}{5}$
(C) $M_C > M_A > M_B$
(D) $M_B > M_A > M_C$

16. Ba^{2+}, CN^- and Co^{2+} form an ionic complex. If this complex is 75% ionized in aqueous solution with van't Hoff factor (i) equal to four and paramagnetic moment is found to be 1.73 BM (due to spin only), then the hybridization state of Co (II) in the complex will be

(A) sp^3d
(B) d^2sp
(C) sp^3d^2
(D) dsp^3

17. A sample of air is saturated with benzene (vapor pressure = 100 mm of Hg at 298 K) at 298 K, 750 mm of Hg pressure. If it is isothermally compressed to one third of its initial volume, the final pressure of the system is

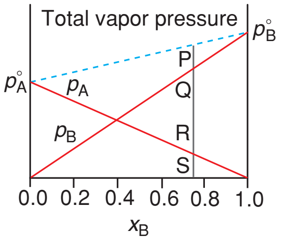
(A) 2250 torr
(B) 2150 torr
(C) 2050 torr
(D) 1950 torr

18. Consider equivocal aqueous solutions of $NaHSO_4$ and NaCl with ΔT_b and $\Delta T_b'$ as their respective boiling point elevations. The value of $\lim_{x\to 0}\frac{\Delta T_b}{\Delta T_b'}$ will be

(A) 1
(B) 1.5
(C) 3.5
(D) 3

Multiple Correct Choice Type

19. Consider the following vapor-pressure composition graph. SP is equal to



(A) PQ + RS
(B) PQ + QR + RS
(C) SR + SQ
(D) PQ + QR

20. For a solution containing non-volatile solute, the relative lowering of vapor pressure is 0.2. If the solution contains 5 moles in all, which of the following statements are true?

(A) Mole fraction of solute in the solution is 0.2.
(B) Number of moles of solute in the solution is 0.2.
(C) Number of moles of solvent in the solution is 4.
(D) Mole fraction of solvent is 0.2.

21. Two liquids A and B form an ideal solution. The solution has a vapor pressure of 700 torr at 80°C. It is distilled till two-third of the solution is collected as condensate. The composition of the condensate is $x'_A = 0.75$ and that of the residue is $x''_A = 0.30$. If the vapor pressure of the residue at 80°C is 600 torr, which of the following is/are true?

(A) The composition of the original liquid was $x_A = 0.6$.
(B) The composition of the original liquid was $x_A = 0.4$.
(C) $p^o_A = \dfrac{2500}{3}$ torr
(D) $p^o_B = 500$ torr

22. For chloroform and acetone or for a solution of chloroform and acetone if p [observed (actual)] is compared with p_s [theoretical (Raoult)], then which of the following is/are true?

(A) $p_s(\text{actual}) < p_s(\text{Raoult})$
(B) $\lim\limits_{x\to 0}[p^o_{\text{acetone}} - p_s(\text{actual})] = 0$
(C) $\lim\limits_{x\to 0}[p^o_{\text{chloroform}} - p_s(\text{actual})] = 0$
(D) $p^o_{\text{acetone}} > p^o_{\text{chloroform}}$ near room temperature

Assertion-Reasoning Type

Choose the correct option from the following:

(A) Statement 1 and Statement 2 are True, Statement 2 is the correct explanation of the Statement 1.
(B) Statement 1 and Statement 2 are True, Statement 2 is NOT a correct explanation of the Statement 1.
(C) Statement 1 is True, Statement 2 is False.
(D) Statement 1 is False, Statement 2 is True.

23. Statement 1: Cooking time is reduced in pressure cooker.
Statement 2: Boiling point of water inside the pressure cooker is elevated.

24. Statement 1: When mercuric iodide is added to the aqueous solution of KI, the freezing point is raised
Statement 2: HgI_2 reacts with KI forming complex ion $(HgI_4)^{2-}$

25. Statement 1: When a cell is placed in hypertonic solution, it shrinks.
Statement 2: Reverse osmosis is used for desalination of water.

26. Statement 1: When *a* mL of a 0.1 molal urea solution is mixed with another *b* mL of 0.1 molal glucose solution, the boiling point of the solution is no different from the boiling points of the samples prior to mixing however, if *a* mL of 0.1 molal urea is mixed with *b* mL of 0.1 molal HF the boiling point of the mixture is different from the boiling points of the separate samples.
Statement 2: HF is an electrolyte (weak) whereas glucose is a non-electrolyte.

Comprehension Type

Paragraph I

According to Raoult's law, partial pressure of any volatile constituent of a solution at a constant temperature is equal to the vapor pressure of pure constituent multiplied by mole fraction of that constituent in the solution.

This law is the major deciding factor whether a solution will be ideal or non-ideal. Ideal solution always obeys Raoult's law at every range of concentration.

A liquid mixture of benzene and toluene is composed of 1 mol of benzene and 1 mol of toluene. Benzene and toluene mixture behave ideally. Given $p^o_t = 4.274$ kN m^{-2}; $p^o_b = 13.734$ kN m^{-2} where subscript t and b stands for toluene and benzene respectively.

27. If the pressure over mixture at 300 K is reduced, at what pressure does the first vapor form?

(A) 18.008 kNm^{-2}
(B) 9.004 kNm^{-2}
(C) 13.05 kNm^{-2}
(D) 3.003 kNm^{-2}

28. What is the composition of first trace of vapor formed in terms of mole-fraction of toluene?

(A) 0.2373
(B) 0.7627
(C) 0.333
(D) 0.67

29. If the pressure is further reduced, at what pressure does last trace of liquid disappear?

(A) 9.004 kN m^{-2}
(B) 6.519 kN m^{-2}
(C) 3.03 kN m^{-2}
(D) None of these

30. What will be the mole fraction of toluene in last trace of liquid?

(A) 0.2373
(B) 0.7627
(C) 0.333
(D) 0.67

Paragraph II

Consider two liquids B and C that form an ideal solution. We hold the temperature fixed at some value T that is above the freezing points of B and C. We shall plot the system's pressure p and against x_B the overall mole fraction of B in the system:

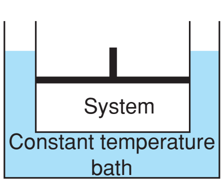
$$x_B = \frac{n_{B\,(\text{total})}}{n_{\text{total}}} = \frac{n_B^l + n_B^v}{n_B^v + n_B^l + n_C^l + n_B^l}$$

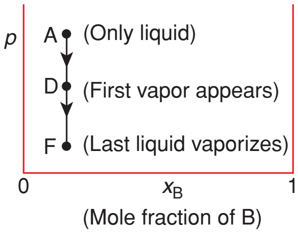
where n_B^l and n_B^v are the number of moles of B in the liquid and vapor phases, respectively. For a close system x_B, is fixed, although n_B^l and n_B^v may vary.

Let the system be enclosed in a cylinder fitted with a piston and immersed in a constant-temperature bath. To see what the p vs. x_B phase diagram looks like, let us initially set the external pressure on the piston high enough for the system to be entirely liquid (point A in below figure). As the pressure is lowered below that at A, the system eventually reaches a pressure where the liquid just begins to vaporize (point D). At point D, the liquid has composition x_B^l, where x_B^l at D is equal to the overall mole fraction x_B since only an infinitesimal amount of liquid has vaporized. What is the composition of the first vapor that comes off? Raoult's law $p_B = x_B^l p_B^o$ relates the vapor phase mole fractions to the liquid composition as follows:

$$x_B^v = \frac{x_B^l p_B^o}{p} \text{ and } x_C^v = \frac{x_C^l p_C^o}{p} \qquad (1)$$

where p_B^o and p_C^o are the vapor pressures of pure B and pure C at T, the system's pressure p equals the sum $p_B + p_C$ of the partial pressures, $x_B^l = \dfrac{n_B^l}{n_B^l + n_C^l}$ and the vapor is assumed ideal.





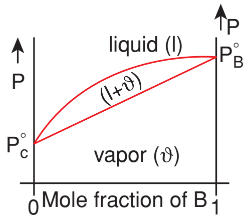
$$\frac{x_B^v}{x_C^v} = \frac{x_B^l p_B^o}{x_C^l p_C^o} \quad \text{Ideal solution} \qquad (2)$$

Let B be the more volatile component, meaning that $p_B^o > p_C^o$. Above equation then shows that $x_B^v/x_C^v > x_B^l/x_C^l$. The vapor above an ideal solution is richer than the liquid in the more volatile component. Equations (1) and (2) apply at any pressure where liquid vapor equilibrium exists, not just at point D.

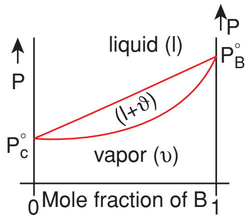
Now let us isothermally lower the pressure below point D, causing more liquid to vaporize. Eventually, we reach point F in figure, where the last drop of liquid vaporizes. Below F, we have only vapor. For any point or the line between D and F liquid and vapor phases coexist in equilibrium.

31. If the above process is repeated for all other compositions of mixture of C and B. If all the points where vapors start converting into liquid are connected and all the points where vapors get completely converted into liquid are connected then obtained graph will look like.

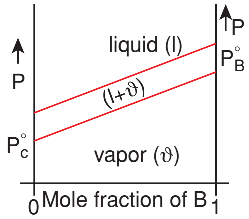
(A)



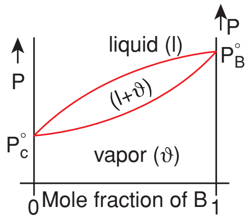
(B)



(C)



(D)



32. The equation of the curve obtained by connecting all those points where the vapors of above mixture (all mixtures of different composition are taken) just start forming will be

(A) $p = p_C^o + (p_B^o - p_C^o)x_B'$

(B) $p = p_C^o + (p_B^o - p_C^o)x_B'$

(C) $p = \dfrac{p_B^o p_C^o}{x_B^o(p_C^o - p_B^o) + p_B^o}$

(D) $p = \dfrac{p_B^o p_C^o}{x_B'(p_C^o - p_B^o) + p_B^o}$

Matrix-Match Type

33. Match the Columns I and II using the information given below:

For an ideal binary liquid solution of A and B, p_A^o = pure vapor pressure of A, p_B^o = pure vapor pressure of B, x_A is the mole fraction of A in liquid phase and y_A = mole fraction of A in vapor phase.

Column I	Column II
(A) $p_A^o > p_B^o$	(p) $x_A = y_A$
(B) Azeotropic mixture	(q) $x_A < y_A$
(C) Equimolar mixture of A and B with $p_A^o < p_B^o$	(r) $x_B < y_B$
(D) Equimolar mixture of A and B with $p_A^o = p_B^o$	(s) $y_B > y_A$

CHEMICAL EQUILIBRIUM

Single Correct Choice Type

1. The normal vapor density of PCl_5 is 104.25. Its vapor density at 250°C when it is 80% dissociated is

(A) 52 (B) 57.9
(C) 86 (D) 120

2. For the equilibrium

$SrCl_2 \cdot 6H_2O(s) \rightleftharpoons SrCl_2 \cdot 2H_2O(s) + 4H_2O(g)$ the equilibrium constant $K_p = 16 \times 10^{-12}$ atm^2 at 1°C. If one liter of air saturated with water vapor at 1°C is exposed to a large quantity of $SrCl_2 \cdot 2H_2O(s)$, what weight of water vapor will be absorbed? Saturated vapor pressure of water at 1°C = 7.6 torr.

(A) 6 g (B) 6.4 mg
(C) 2.3 g (D) 8.5 g

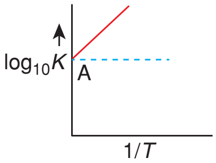
3. A 10 L box contains O_3 and O_2 at equilibrium at 2000 K. For $2O_3(g) \rightleftharpoons 3O_2(g)$ $K_p = 4 \times 10^{14}$ atm^2. Assume that $p_{O_2} \gg p_{O_3}$ and if total pressure is 8 atm, then partial pressure of O_3 will be

(A) 8×10^{-5} atm (B) 11.3×10^{-7} atm
(C) 9.71×10^{-6} atm (D) 9.71×10^{-2} atm

4. Nitrogen gas was injected into an equilibrium mixture of $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$. The pressure is increased from 1.0 atm to 10 atm. Which of the following statements is correct?

(A) The concentration of the reacting gases is unchanged.
(B) $[SO_3]$ increases.
(C) $[SO_2]$ increases.
(D) $[O_2]$ increases.

5. Variation of $\log_{10}K$ with $1/T$ is shown by the following graph in which straight line is at 45°. Hence ΔH^o is



(A) +4.606 cal (B) –4.606 cal
(C) 2 cal (D) –2 cal

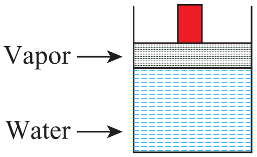
6. The equilibrium constant for,
$2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g)$ is 0.0118 at 1200 K while the heat of dissociation is 597.4 kJ. The standard equilibrium constant of the reaction at 1300 K is

(A) 1.180
(B) 11.80
(C) 118.0
(D) cannot be calculated from given data

7. When a bottle of cold drink is opened, the gas comes out with a fizz due to

(A) decrease in temperature.
(B) increase in pressure.
(C) decrease in pressure suddenly which results in decrease of solubility of CO_2 gas in water.
(D) None of these.

8. Some quantity of water is contained in a container as shown in the following figure. As neon is added to this system at constant pressure, the amount of liquid water in the vessel



(A) increases.
(B) decreases.
(C) remains same.
(D) changes unpredictably.

9. If β_1, β_2 and β_3 are stepwise formation constants of MCl, MCl_2, MCl_3 and K is the overall formation constant of MCl_3, then

(A) $K = \beta_1 + \beta_2 + \beta_3$

(B) $\frac{1}{K} = \frac{1}{\beta_1} + \frac{1}{\beta_2} + \frac{1}{\beta_3}$

(C) $\log K = \log \beta_1 + \log \beta_2 + \log \beta_3$
(D) $pK = \log \beta_1 + \log \beta_2 + \log \beta_3$

10. At a temperature T, a compound $AB_4(g)$ dissociates as $2AB_4(g) \rightleftharpoons A_2(g) + 4B_2(g)$ with a degree of dissociation x, which is small compared with unity. The expression of K_p in terms of x and total pressure p is

(A) $8p^3x^5$
(B) $256\, p^3x^5$
(C) $4px^2$
(D) None of these

11. In a system $A(s) \rightleftharpoons 2B(g) + 3C(g)$, if the concentration of C at equilibrium is increased by a factor of 2, it will cause the equilibrium concentration of B to change to

(A) two times the original value.
(B) one half of its original value.
(C) $\dfrac{1}{\sqrt{2}}$ times its original value.
(D) $\dfrac{1}{2\sqrt{2}}$ times.

12. In an aqueous solution of volume 500 mL, when the reaction $2Ag^+ + Cu \rightleftharpoons Cu^{2+} + 2Ag$ reached equilibrium, the $[Cu^{2+}]$ was x M. When 500 mL of water is further added, at the equilibrium $[Cu^{2+}]$ will be

(A) $2x$ M
(B) x M
(C) between xM and $x/2$ M
(D) less then $x/2$ M

13. One mole of mixture of N_2, NO_2 and N_2O_4 has a mean molar mass of 55.4. On heating to a temperature at which all the N_2O_4 may be presumed to have dissociated: $N_2O_4 \rightleftharpoons 2NO_2$, the mean molar mass tends to the lower value of 39.6. What is the mole ratio of $N_2 : NO_2 : N_2O_4$ in the original mixture?

(A) 0.5 : 0.1 : 0.4
(B) 0.6 : 0.1 : 0.3
(C) 0.5 : 0.2 : 0.3
(D) 0.6 : 0.2 : 0.2

14. For the reaction: $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$, the degree of dissociation (α) of HI(g) is related to equilibrium constant K_p by the expression

(A) $\dfrac{1+2\sqrt{K_p}}{2}$
(B) $\sqrt{\dfrac{1+2K_p}{2}}$
(C) $\sqrt{\dfrac{2K_p}{1+2K_p}}$
(D) $\dfrac{2\sqrt{K_p}}{1+2\sqrt{K_p}}$

15. Densities of diamond and graphite are 3.5 and 2.3 g mL^{-1}

$$C(\text{diamond}) \rightleftharpoons C(\text{graphite}); \quad \Delta_r H = -1.9 \text{ kJ mol}^{-1}$$

favorable conditions for formation of diamond are

(A) high pressure and low temperature.
(B) low pressure and high temperature.
(C) high pressure and high temperature.
(D) low pressure and low temperature.

Multiple Correct Choice Type

16. An industrial fuel, water gas, which consists of a mixture of H_2 and CO can be made by passing steam over red-hot carbon. The reaction is

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$$
$$\Delta H = +131 \text{ kJ}$$

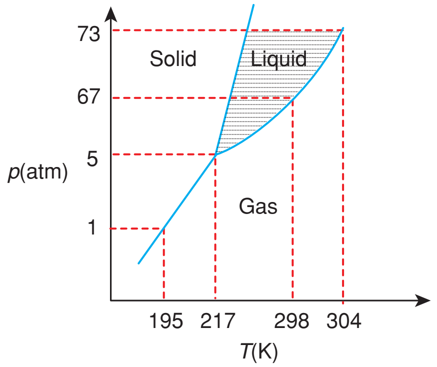
The yield of CO and H_2 at equilibrium would be shifted to the product side by

(A) raising the relative pressure of the steam.
(B) adding hot carbon.
(C) raising the temperature.
(D) reducing the volume of the system.

17. Which of the following do not change the value of K for a reaction?

(A) Addition of catalyst.
(B) Increase in temperature.
(C) Increase in pressure.
(D) Removal of one of the products.

18. Phase diagram of CO_2 is shown in the following figure.



Based on the above, identify the correct statement(s).

(A) 298 K is the normal boiling point of liquid CO_2.
(B) At 1 atm and 190 K, CO_2 will exist as gas.

(C) $CO_2(s)$ will sublime above 195 K under normal atmospheric pressure.
(D) Melting point and boiling point of CO_2 will increase on increasing pressure.

Assertion-Reasoning Type

Choose the correct option from the following:

(A) Statement 1 and Statement 2 are True, Statement 2 is the correct explanation of the Statement 1.
(B) Statement 1 and Statement 2 are True, Statement 2 is NOT a correct explanation of the Statement 1.
(C) Statement 1 is True, Statement 2 is False.
(D) Statement 1 is False, Statement 2 is True.

19. **Statement 1:** The effect of temperature on equilibrium constant is given by van't Hoff''s equation.
Statement 2: van't Hoff's equation is

$$\log \frac{K_1}{K_2} = \frac{\Delta H^\circ}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right].$$

20. **Statement 1:** The value of K increases when concentration of the reactants is increased.
Statement 2: With increase in concentration of reactants, the equilibrium shifts in forward direction.

21. **Statement 1:** For a reaction, concentration quotient Q is equal to K when the reaction is in equilibrium.
Statement 2: If a catalyst is added to the reaction at equilibrium, the value of Q_C not equal to K_C.

Comprehension Type

Paragraph I

When a reversible reaction is carried out in a closed vessel, a stage is reached when the forward and the backward reactions proceed with the same rate. This stage is known as chemical equilibrium. Following are the equilibriums at 0ºC.

$SrCl_2 \cdot 6H_2O(s) \rightleftharpoons SrCl_2 \cdot 2H_2O(s) + 4H_2O(g)$; $K_p = 1.6 \times 10^{-15}$

$Na_2HPO_4 \cdot 12H_2O(s) \rightleftharpoons Na_2HPO_4 \cdot 7H_2O(s) + 5H_2O(g)$; $K_p = 2.43 \times 10^{-8}$

$Na_2SO_4 \cdot 10H_2O(s) \rightleftharpoons Na_2SO_4(s) + 10H_2O(g)$; $K_p = 10^{-30}$

The vapor pressure of water at 0ºC is 4.58 torr.

22. Which is most effective drying agent at 0ºC?

(A) $SrCl_2 \cdot 2H_2O(s)$
(B) $Na_2HPO_4 \cdot 7H_2O(s)$
(C) $Na_2SO_4(s)$
(D) All equally

23. $Na_2SO_4 \cdot 10H_2O(s)$ will be efflorescent when exposed to the air at 0ºC at

(A) pressure below 0.76 torr.
(B) pressure above 0.76 torr.
(C) pressure above 4.58 torr.
(D) pressure equal to 0.76 torr.

24. At what relative humidity will Na_2SO_4 be deliquescent (absorb moisture) when exposed to the air at 0ºC?

(A) Below 16.59% (B) Above 16.59%
(C) Above 39.5% (D) Below 39.5%

Paragraph II

The equilibrium state gets affected if temperature, pressure or concentration is changed. This was studied by Le Chatelier in 1885. According to this principle, "at equilibrium, the change in temperature, pressure or concentration will shift the equilibrium towards the direction where the effect of the change gets neutralized."

If temperature is increased at equilibrium, the equilibrium will be shifted towards the direction where effect of temperature will be neutralized that is, where heat is absorbed. Backward reaction is endothermic, thus equilibrium will shift towards the direction, so that heat is absorbed.

On increasing the pressure, equilibrium will shift towards the direction where volume is decreased.

Concentration of product will increase to neutralize the effect of adding reactant in an equilibrium reaction, that is, equilibrium will shift towards forward direction.

25. In a reversible reaction $K_C > K_p$ and $\Delta H = +40$ kcal. The product will be obtained in less amount on

(A) decreasing pressure and temperature.
(B) increasing pressure and temperature.
(C) decreasing pressure and increasing temperature.
(D) decreasing temperature and increasing pressure.

26. Which of the following factors will be favorable for higher yields of NO in the reaction given below?

$$N_2 + O_2 \rightleftharpoons 2NO(g)\ (\Delta H = +ve)$$

(A) Low temperature, high pressure and high concentration of N_2 and O_2.
(B) High temperature, and high concentrations of N_2 and O_2. The reaction remains unaffected by pressure.
(C) High temperature, low pressure and low concentration of N_2 and O_2.
(D) Low temperature, low pressure and high concentration of N_2 and O_2.

27. Which of the following conditions should be more favorable for increasing the rate of forward reaction in the equilibrium given below?

$$H_2 \rightleftharpoons H + H$$

(A) 2000ºC temperature and 760 mm pressure.
(B) 3500ºC temperature and 100 cm pressure.
(C) 3500ºC temperature 1 mm pressure.
(D) None of the above.

Matrix-Match Type

28. Match the reaction with the parameter which changes to shift the direction of equilibrium.

Column I	Column II
(A) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	(p) Pressure
(B) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$	(q) Temperature
(C) $H_2O(l) \rightleftharpoons H_2O(g)$	(r) Volume
(D) $H_2O(s) \rightleftharpoons H_2O(l)$	(s) Addition of inert gas at constant p

29. Match the reaction with the characteristic of chemical equilibrium.

Column I	Column II
(A) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$	(p) K_p does not exist
(B) $CH_3COOC_2H_5(aq) + H_2O \rightleftharpoons CH_3COOH(aq) + C_2H_5OH(aq)$	(q) Homogeneous equilibrium
(C) $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$	(r) Heterogeneous equilibrium
(D) $A(aq) + B(s) \rightleftharpoons C(g) + D(g)$	(s) $K_p = K_C$

IONIC EQUILIBRIUM

Single Correct Choice Type

1. Choose the incorrect statement

(A) In water, all the strong acids are equally strong so water is called levelling solvent.
(B) H_3BO_3 is a Lewis acid.
(C) H_3BO_3 is an Arrhenius acid.
(D) Due to high charge density, H^+ ion in water is extremely hydrated in the form of H_3O^+, $H_5O_2^+$, $H_7O_3^+$.

2. pOH of H_2O is 7.0 at 298 K. If water is heated at 350 K, then, which of the following statement should be true?

(A) pOH will decrease.
(B) pOH will increase.
(C) pOH will remain 7.0.
(D) Concentration of H^+ ions will increase but that of OH^- will decrease.

3. Calculate $[S^{2-}]$ in 0.1 M H_2S solution. (Given: $K_{a1} = 10^{-7}$ and $K_{a2} = 10^{-14}$)

(A) 10^{-7} (B) 10^{-14}
(C) 2×10^{-14} (D) 10^{-21}

4. Calculate pH of a solution obtained by mixing equal volumes of 0.02 M HOCl and 0.2 M CH_3COOH solution. (Given: $K_{a(HOCl)} = 2\times10^{-4}$, $K_{a(CH_3COOH)} = 2\times10^{-5}$)

(A) 2.7 (B) 3.7
(C) 2.4 (D) 3.5

5. pH of a solution containing 0.1 M HCl and 0.001 M CH_3COOH (Given: $K_a = 2 \times 10^{-5}$) is

(A) 1 (B) 2
(C) 3 (D) 1.5

6. Calculate pH of 10^{-2}M $Ba(Lac)_2$. (Given: $K_{a(\text{lactic acid})} = 10^{-4}$)

(A) 8.15 (B) 8.56
(C) 8.23 (D) 9.4

7. What is the pH of 0.1 M $NaHCO_3$, if $K_1 = 4.5 \times 10^{-7}$, $K_2 = 4.5 \times 10^{-11}$ for carbonic acids? (Given: log 2 = 0.3, log 3 = 0.48)

(A) 8.34 (B) 8.6
(C) 8.2 (D) 8.9

8. Calculate buffer capacity of 1 L of a mixture of 0.1 M CH_3COOH and 0.1 M CH_3COONa. (Given: $pK_{a(CH_3COOH)} = 4.74$)

(A) 2.303×0.05 (B) 0.1×2.303
(C) 1×2.303 (D) None of these

9. From a weak acid of pK_a = 6, the pH range of practically possible buffer solution is

(A) 5 to 7 (B) 6 to 8
(C) 5 to 6 (D) 6 to 7

10. What fraction of an indicator HIn is in the basic form at a pH of 6 if the pK_a of the indicator is 5?

(A) $\frac{1}{2}$ (B) $\frac{1}{11}$
(C) $\frac{10}{11}$ (D) $\frac{1}{10}$

11. At what minimum concentration of OH^- will 10^{-3} mol of $Zn(OH)_2$ go into solution as $Zn(OH)_4^{2-}$ in 1 L solution?

Given:

$$Zn(OH)_4^{2-}(aq) \rightleftharpoons Zn^{2+}(aq) + 4OH^-(aq);$$
$K = 10^{-15}$

$$Zn(OH)_2(s) \rightleftharpoons Zn^{2+}(aq) + 2OH^-(aq);$$
$K_{sp} = 10^{-17}$

(A) 0.316 M (B) 0.512 M
(C) 0.225 M (D) None of these

12. The solubility of silver oxalate in 10^{-2} M potassium oxalate solution is (Given: $K_{sp(Ag_2CrO_4)} = 10^{-10}$)

(A) 5×10^{-5} (B) 4×10^{-4}
(C) 3×10^{-3} (D) 2×10^{-2}

13. Calculate the solubility of AgCl in 2.7 M NH_3 solution. (Given: $K_{sp(AgCl)} = 10^{-10}$ and K_f $[Ag(NH_3)_2]^+ = 1.6 \times 10^7$)

(A) 0.1 mol L^{-1} (B) 0.2 mol L^{-1}
(C) 0.01 mol L^{-1} (D) None of these

14. At 25°C the solubility product of $BaCO_3$ is 1.6×10^{-8} $(mol\,dm^{-3})^2$ and that of $BaSO_4$ is 9×10^{-10} $(mol\,dm^{-3})^2$. If pure water is shaken up with the pure solids, $BaCO_3$ and $BaSO_4$ at 25ºC till equilibrium is reached, what is the concentration of Ba^{2+} ion in solution in mol dm^{-3}?

(A) 3.9×10^{-4} M (B) 1.3×10^{-4} M
(C) 3.9×10^{-5} M (D) 1.3×10^{-5} M

15. Arrange the solubility of AgBr in the given solution in increasing order.

(I) 0.1 M NH_3 (II) 0.1 M $AgNO_3$
(III) 0.2 M NaBr (IV) pure water

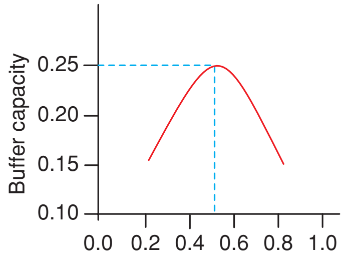
(A) (III) < (II) < (IV) < (I)
(B) (III) < (II) < (I) < (IV)
(C) (III) < (II) = (I) < (IV)
(D) (II) < (III) < (IV) < (I)

16. At what molar concentration of HCl will its aqueous solution have an $[H^+]$ to which equal contributions come from HCl and H_2O?

(A) $\sqrt{60} \times 10^{-7}$ M
(B) $\sqrt{50} \times 10^{-8}$ M
(C) $\sqrt{40} \times 10^{-9}$ M
(D) $\sqrt{30} \times 10^{-8}$

17. A buffer solution is prepared by mixing *a* moles of CH_3COONa and *b* moles of CH_3COOH such that $(a + b) = 1$, into water to make 1 L buffer solution. If the buffer capacity of this buffer solution is plotted against moles of salt CH_3COONa (with *a*) then the plot obtained will be (to the scale) approximately.

(A)



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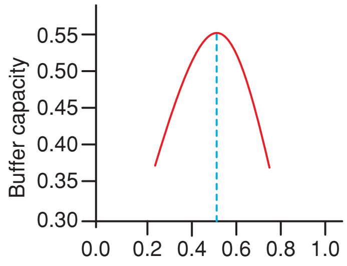

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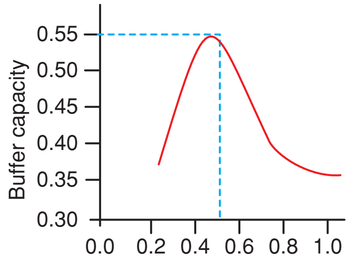

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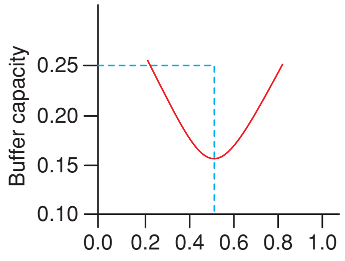


18. The solubility product of $Mg(OH)_2$ in water at 25ºC is 2.56×10^{-13} $(mol\,dm^{-3})^3$ while that of

$Al(OH)_3$ is 4.32×10^{-34} $(\text{mol dm}^{-3})^4$. If S_1 and S_2 are the solubilities of $Mg(OH)_2$ and $Al(OH)_3$ in water in mol dm^{-3} at 25°C, what is range of the ratio, S_1/S_2?

(A) 10^5 (B) 10^4
(C) 10^6 (D) 10^3

19. Which of the following statements is correct for a solution saturated with AgCl and AgBr if their solubilities in moles per liter in separate solutions are x and y respectively?

(A) $[Ag^+] = x + y$
(B) $[Ag^+] = [Br^-] + [Cl^-]$
(C) $[Br^-] = y$
(D) $[Cl^-] > x$

20. 0.2 millimoles of Zn^{2+} ion is mixed with $(NH_4)_2S$ of molarity 0.02 M. The amount of Zn^{2+} that remains unprecipitated in 20 mL of this solution would be (Given: K_{sp} of ZnS $= 4 \times 10^{-24}$)

(A) 5.2×10^{-22} g
(B) 2.6×10^{-22} g
(C) 2×10^{-23} g
(D) None of these

21. Which one of the following is the correct expression for the solution containing n number of weak acids?

(A) $[H^+] = \sqrt{\sum_{i=1}^{n} \frac{K_i}{C_i}}$ (B) $[H^+] = \sqrt{\sum_{i=1}^{n} K_i C_i}$

(C) $[H^+] = \sum_{i=1}^{n} K_i C_i$ (D) None of these

22. The pH of glycine at the first half equivalence point is 2.34 and that at second half equivalence point is 9.60. At the equivalence point (the first inflection point), the pH is

(A) 3.63 (B) 2.34
(C) 5.97 (D) 11.94

23. 30 mL of 0.06 M solution of the protonated form of an anion acid methionine (H_2A^+) is treated with 0.09 M NaOH. Calculate pH after addition of 20 mL of base. $pK_{a1} = 2.28$ and $pK_{a2} = 9.2$.

(A) 5.5 (B) 5.74
(C) 9.5 (D) None

24. A sample of water has hardness expressed as 80 ppm of Ca^{2+}. This sample is passed through an ion exchange column and the Ca^{2+} is replaced by H^+. What is the pH of the water after it has been so treated? [Atomic mass of Ca = 40]

(A) 3 (B) 2.7
(C) 5.4 (D) 2.4

Multiple Correct Choice Type

25. 100 mL of 0.5 M hydrazoic acid (HN_3, $K_a = 3.6 \times 10^{-4}$) and 400 mL of 0.1 M cyanic acid (HOCN, $K_a = 8 \times 10^{-4}$) are mixed. Which of the following is (are) true for the final solution?

(A) $[H^+] = 10^{-2}$
(B) $[N_3^-] = 3.6 \times 10^{-3}$
(C) $[OCN^-] = 4.571 \times 10^{-3}$
(D) $[H^+] = 1.4 \times 10^{-2}$

26. When 0.1 mol arsenic acid H_3AsO_4 is dissolved in 1 L buffer solution of pH = 8, which of the following hold good? (Given: $K_1 = 2.5 \times 10^{-4}$, $K_2 = 5 \times 10^{-8}$, $K_3 = 2 \times 10^{-13}$ for arsenic acid.) [$\ll$ sign denotes that the high concentration is at least more than 100 times the lower one]

(A) $[H_3AsO_4] \ll [H_2AsO_4^-]$
(B) $[H_2AsO_4^-] \ll [HAsO_4^{2-}]$
(C) $[HAsO_4^{2-}] \ll [H_2AsO_4^-]$
(D) $[AsO_4^{3-}] \ll [HAsO_4^{2-}]$

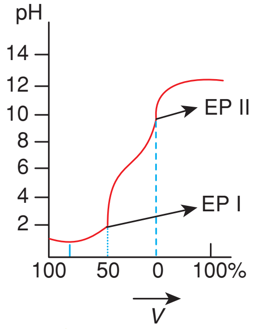
27. Let the color of the indicator HIn (colorless) be visible only when its ionized form (pink) is 25% or more in a solution. When HIn ($pK_a = 9.0$) is added to a solution of pH = 9.6, predict what will happen? (Take log 2 = 0.3)

(A) Pink color will be visible.
(B) Pink color will not be visible.
(C) % age of ionized form will be less than 25%.
(D) % age of ionized form will be more than 25%.

28. Which of the following mixtures will act as a buffer?

(A) H_2CO_3 + NaOH (1.5 : 1 molar ratio)
(B) H_2CO_3 + NaOH (1.5 : 2 molar ratio)
(C) NH_4OH + HCl (5 : 4 molar ratio)
(D) NH_4OH + HCl (4 : 5 molar ratio)

29. A weak acid (or base) is titrated against a strong base (or acid), volume V of strong base (or acid) is plotted against pH of the solution. The weak protolyte (i.e. acid or base) could be



(A) Na_2CO_3 (B) $Na_2C_2O_4$
(C) $H_2C_2O_4$ (D) $CH_2(COOH)_2$

30. The variation of pH during the titration of 0.5 N Na_2CO_3 with 0.5 N HCl is shown in the graph in Question 29. The following table indicates the color and pH ranges of different indicators:

Indicator	Range of color change	Color in acid	Color in base
Thymol blue	1.2 to 2.8	Red	Yellow
Bromocresol red	4.2 to 6.3	Red	Yellow
Bromothymol blue	6.0 to 7.6	Yellow	Blue
Cresolphzthalein	8.2 to 9.8	Colorless	Red

Based on the graph and the table, which of the following statements are true?

(A) The first equivalence point (EP I) can be detected by cresolphthalein.
(B) The complete neutralization can be detected by bromothymol blue.
(C) The second equivalence point (EP I) can be detected by bromocresol red.
(D) The volume of HCl required for the first equivalence point is half the volume of HCl required for the second equivalence point.

31. Which of the following solutions when added to 1 L of a 0.1 M CH_3COOH solution will cause no change in either the degree of dissociation of CH_3COOH or the pH of the solution? $K_a = 1.8 \times 10^{-5}$ for CH_3COOH.

(A) 3 mM HCOOH ($K_a = 6 \times 10^{-4}$)
(B) 0.1 M CH_3COONa
(C) 1.34 mM HCl
(D) 0.1 M CH_3COOH

32. Buffer solution A of a weak monoprotic acid and its sodium salt in the concentration ratio $x : y$ has pH = $(pH)_1$. Buffer solution B of the same acid and its sodium salt in the concentration ratio $y : x$ has pH = $(pH)_2$. If $(pH)_2 - (pH)_1$ =1unit and $(pH)_1 + (pH)_2 = 9.5$ units, then

(A) $pK_a = 4.75$ (B) $\frac{x}{y} = 2.36$
(C) $\frac{x}{y} = 3.162$ (D) $pK_a = 5.25$

Assertion-Reasoning Type

Choose the correct option from the following:

(A) Statement 1 and Statement 2 are True, Statement 2 is the correct explanation of the Statement 1.
(B) Statement 1 and Statement 2 are True, Statement 2 is NOT a correct explanation of the Statement 1.
(C) Statement 1 is True, Statement 2 is False.
(D) Statement 1 is False, Statement 2 is True.

33. **Statement 1:** A solution containing acetic acid and sodium acetate in equimolar quantities can act as a buffer solution.
Statement 2: The pH of the above mentioned buffer would be equal to pK_a of acetic acid.

34. **Statement 1:** Aqueous solutions of all strong acids contain only the same acid, the hydronium ion.
Statement 2: Hydronium ion is the strongest acid that can exist in any significant concentration in dilute aqueous solution.

35. **Statement 1:** Solubility of $BaSO_4$ in 0.1 M Na_2SO_4 is 10^{-9} M, hence its K_{sp} is 10^{-18}.
Statement 2: Because for $BaSO_4$ $K_{sp} = (S)^2$ [symbols have their usual meanings].

36. **Statement 1:** It is difficult to distinguish the strengths of the strong acids such as HCl, H_2SO_4, HNO_3, HBr, HI or $HClO_4$ in dilute aqueous solutions.
Statement 2: In dilute aqueous solution all strong acids donate a proton to water and are essentially 100% ionized to produce a solution containing H_3O^+ ions plus the anions of strong acid.

Comprehension Type

Paragraph I

Consider a solution of CH_3COONH_4 which is a salt of weak acid and weak base. The equilibrium involved in the solution is

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^- \quad (1)$$
$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+ \quad (2)$$
$$H^+ + OH^- \rightleftharpoons H_2O \quad (3)$$

If we add these three reactions, then the net reaction is

$$CH_3COO^- + NH_4^+ + H_2O \rightleftharpoons CH_3COOH + NH_4OH \quad (4)$$

Both CH_3COO^- and NH_4^+ get hydrolyzed independently and their hydrolysis depends on

(i) their initial concentration
(ii) the value of K_h which is $\frac{K_w}{K_a}$ for CH_3COO^- and $\frac{K_w}{K_b}$ for NH_4^+

Since both of the ions were produced from the same salt, their initial concentrations are same. Therefore unless and until the value of K_w/K_a and K_w/K_b or K_a and K_b is same, the degree of hydrolysis of ion cannot be the same.

To explain why, we assume that degree of hydrolysis of cation and anion is the same, we need to now look at the third reaction, that is, combination of H^+ and OH^- ions. It is obvious that this reaction happens only because one reaction produced H^+ ion and the other produced OH^- ions. We can also note that this reaction causes both the hydrolysis reaction to occur more since their product ions are being consumed. Keep this thing in mind that the equilibrium which has smaller value of equilibrium constant is affected more by the common ion effect. For the same reason if for any reason a reaction is made to occur to a greater extent by the consumption of any one of the product ion, the reaction with the smaller value of equilibrium constant tends to get affected more.

Therefore we conclude that firstly the hydrolysis of both the ions occurs more in the presence of each other (due to consumption of the product ions) than in each other is absence. Secondly the hydrolysis of the ion which occurs to a lesser extent (due to smaller value of K_h) is affected more than the one whose K_h is greater. Hence, we can see that the degree of hydrolysis of both the ions would be close to each other when they are getting hydrolyzed in the presence of each other.

37. In the hydrolysis of salt of weak acid and weak base

(A) degree of hydrolysis of cation and anion is different.
(B) degree of hydrolysis of cation and anion is same.
(C) degree of hydrolysis of cation and anion is different and they can never be assumed same.
(D) degree of hydrolysis of cation and anion is different but they are very close to each other when they are getting hydrolyzed in the presence of each other.

38. For 0.1 M CH_3COONH_4 salt solution, given, $K_{a(CH_3COOH)} = K_{b(NH_4OH)} = 2 \times 10^{-5}$. In this case, degree of hydrolysis of cation and anion is

(A) exactly same.
(B) slightly different.
(C) cannot to be determined
(D) different but can be take approximately same.

39. In a solution of $NaHCO_3$, the amphiprotic anion can under ionization to form H^+ ion and hydrolysis to form OH^- ion.

$$HCO_3^- + H_2O \xrightleftharpoons{\text{ionization}} CO_3^{2-} + H_2O$$

$$HCO_3^- + H_2O \xrightleftharpoons{\text{hydrolysis}} H_2CO_3 + OH^-$$

To calculate pH, suitable approximation is

(A) $[CO_3^{2-}] = [H_2CO_3]$
(B) degree of ionization = degree of hydrolysis
(C) both (A) and (B)
(D) neither (A) nor (B)

Paragraph II

When aluminium salts are added to water, Al^{3+} ions are immediately attracted to the negative end of polar water molecules. They form hexaaquaaluminum (III) ions, $[Al(H_2O)_6]^{3+}$. This is often written simply as $Al^{3+}(aq)$. However the electric field associated with small, highly charged Al^{3+} ion is so intense that it draws electrons in the O–H bonds of water towards itself. This enables the water molecules to become donors. In aqueous solution, free water molecules act as bases and the following equilibrium is established.

$$[Al(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Al(OH)(H_2O)_5]^{2+} + H_3O^+$$

Thus, solutions of Al^{3+} salts are acidic, in fact as acidic as vinegar. When a base stronger than H_2O, (e.g., S^{2-}) is added to aqueous aluminium salts further H^+ ions are removed from $[Al(H_2O)_6]^{3+}$ and insoluble aluminium hydroxide precipitates.

$$2[Al(H_2O)_6]^{3+}(aq) + 3S^{2-}(aq) \rightarrow 2[Al(OH)_3(H_2O)_3](s) + 3H_2S(g)$$

A stronger base can remove $4H^+$ ions as follows:

$$[Al(H_2O)_6]^{3+} + 4OH^- \rightleftharpoons [Al(OH)_4(H_2O)]^-(aq) + 4H_2O(l)$$

40. Which of $[Al(H_2O)_6]^{3+}$, H_2S or H_2O is the strongest acid ?

(A) $[Al(H_2O)_6]^{3+}$
(B) H_2S
(C) H_2O
(D) All are the same.

41. A base which will behave just like S^{2-} is

(A) CO_3^{2-}
(B) CH_3OH
(C) NH_4^+
(D) NH_2^-

42. Another ion that would behave similar to Al^{3+} (aq) in forming an acidic solution is

(A) $Be_4^{2+}(aq)$
(B) $Ba^{2+}(aq)$
(C) Na^+
(D) Tl^+

43. $[Al(OH)_3(H_2O)_3](s)$ more simply written as $Al(OH)_3(s)$ is

(A) acidic. (B) basic.
(C) neutral. (D) amphoteric.

44. Which gas would get absorbed when passed into a solution of $Al^{3+}(aq)$?

(A) NH_3 (B) NO
(C) CO (D) O_2

Matrix-Match Type

45. Match the ions with their characteristic behavior.

Column I	Column II
(A) Cation hydrolysis	(p) NH_2^-
(B) No hydrolysis	(q) PH_4^+
(C) Complete hydrolysis	(r) O^{2-}
(D) Conjugate base of NH_3	(s) Na^+
	(t) CN^-

46. If we mix equal volumes of two solutions, match with the pH of resulting solution.

Column I	Column II
(A) 0.2 M KOH + 0.5 M HCOOH	(p) 0.7
(B) 0.1 M NaC1 + 0.1 M $NaNO_3$	(q) between 1 to 7
(C) 0.1 NI NH_4CI + 0.1 M NaOH	(r) 7
(D) 0.5 M HCI + 0.1 M NH_4OH	(s) greater than 7

47. K_1 and K_2 are first and second ionization constant of H_2CrO_4, K_3 is dissociation constant for NH_3. Match the buffer action with the corresponding equation.

Column I	Column II
(A) 0.1 M H_2CrO_4	(p) $pH = 7 + 1/2\ pK_2 - 1/2\ pK_3$
(B) 0.1 M $KHCrO_4$	(q) $pH = 7 + 1/2\ pK_2 + 1/2 \log C$
(C) 0.1 M $(NH_4)_2\ CrO_4$	(r) $pH = 1/2\ pK_1 - 1/2 \log C$
(D) 0.1 M K_2CrO_4	(s) $pH = 1/2\ (pK_1 + pK_2)$

ELECTROCHEMISTRY

Single Correct Choice Type

1. The specific conductivity of a saturated solution of AgCl is 3.40×10^{-6} ohm^{-1} cm^{-1} at 25ºC. If $\lambda_{Ag^+} = 62.3\ ohm^{-1}\ cm^2\ mol^{-1}$ and $\lambda_{Cl^-} = 67.7\ ohm^{-1}\ cm^2\ mol^{-1}$, the solubility of AgCl at 25ºC is

(A) 2.6×10^{-5} mol L^{-1}
(B) 3.731×10^{-3} mol L^{-1}
(C) 3.731×10^{-5} mol L^{-1}
(D) 2.6×10^{-3} g L^{-1}

2. If $E^o_{Fe^{2+}/Fe}$ is x_1, $E^o_{Fe^{3+}/Fe}$ is x_2 then $E^o_{Fe^{3+}/Fe^{2+}}$ will be

(A) $3x_2 - 2x_1$ (B) $x_2 - x_1$
(C) $x_2 + x_1$ (D) $2x_1 + 3x_2$

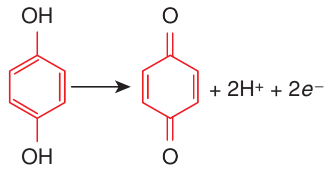
3. For the cell Pt | Cl_2 (p_1) | HCl (0.1 M) | Pt | Cl_2 (p_2); cell reaction will be spontaneous if

(A) $p_1 = p_2$ (B) $p_1 > p_2$
(C) $p_2 > p_1$ (D) $p_1 = p_2 = 1$ atm

4. If the solution of the $CuSO_4$ in which copper rod is immersed is diluted to 10 times, the oxidation electrode potential

(A) increases by 0.030 V.
(B) decreases by 0.030 V.
(C) increases by 0.059 V.
(D) decreases by 0.0059 V.

5. At pH = 2, $E_{Quinhydrone}$ will be (Given: $E^o_{Quinhydrone}$ = 1.30 V)



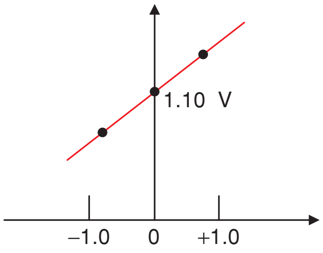
(A) 1.36 V (B) 1.30 V
(C) 1.42 V (D) 1.20 V

6. Which graph correctly correlates E_{cell} as a function of concentrations for the cell (for different values of M and M′)?

$Zn(s) + Cu^{2+}(M) \longrightarrow Zn^{2+}(M') + Cu(s)$; $E^o_{cell} = 1.10$ V

x-axis: $\log_{10} \dfrac{[Zn^{2+}]}{[Cu^{2+}]}$, y-axis: E_{cell}

(A)



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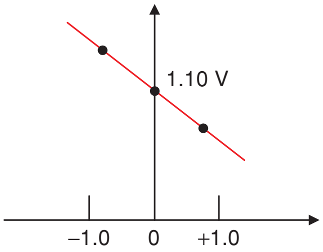

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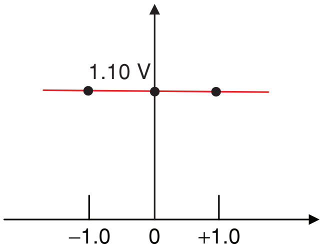

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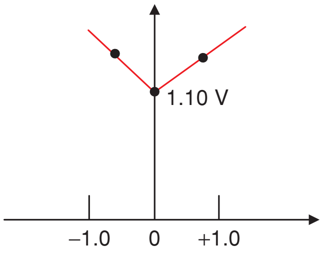


7. The standard emf of the cell, Cd(s) | $CdCl_2$(aq) || AgCl(s) | Ag(s) in which the cell reaction is, $Cd(s) + 2AgCl(s) \rightarrow 2Ag(s) + Cd^{2+}(aq) + 2Cl^-(aq)$ is 0.6915 V at 0°C and 0.6753 V at 25°C. The ΔH of the reaction at 25°C is

(A) –176 kJ (B) –234.7 kJ
(C) +123.5 kJ (D) –167.26 kJ

8. In electrolysis of an aqueous solution of sodium sulphate, 2.4 L of oxygen at STP was liberated at anode. The volume of hydrogen at STP liberated at cathode would be

(A) 1.2 L (B) 2.4 L
(C) 2.6 L (D) 4.8 L

9. A current of 0.75 A is passed through an acidic solution of $CuSO_4$ for 10 min. The volume of oxygen liberated at anode (at STP) will be

(A) 0.261 dm^3 (B) 0.261 cm^3
(C) 0.261×10^2 mL (D) 0.261 m^3

10. A current of 9.65 A is drawn from a Daniell cell for exactly 1 h. If molar masses of Cu and Zn are 63.5 g mol^{-1} and 65.4 g mol^{-1} respectively, the loss in mass at anode and gain in mass at cathode, respectively, are

(A) 11.43 g, 11.77 g (B) 11.77 g, 11.43 g
(C) 22.86 g, 23.4 g (D) 23.54 g, 22.86 g

11. The following facts are available

$$2X^- + Y_2 \longrightarrow 2Y^- + X_2$$
$$2W^- + Y_2 \longrightarrow \text{No reaction}$$
$$2Z^- + X_2 \longrightarrow 2X^- + Z_2$$

Which of the following statements is correct?

(A) $E^o_{W^-/W_2} > E^o_{Y^-/Y_2} > E^o_{X^-/X_2} > E^o_{Z^-/Z_2}$

(B) $E^o_{W^-/W_2} < E^o_{Y^-/Y_2} < E^o_{X^-/X_2} < E^o_{Z^-/Z_2}$

(C) $E^o_{W^-/W_2} < E^o_{Y^-/Y_2} > E^o_{X^-/X_2} > E^o_{Z^-/Z_2}$

(D) $E^o_{W^-/W_2} > E^o_{Y^-/Y_2} < E^o_{X^-/X_2} < E^o_{Z^-/Z_2}$

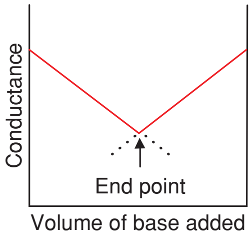
12. A hydrogen electrode placed in a buffer solution of CH_3COONa and CH_3COOH in the ratios of $x : y$ and $y : x$ has electrode potential values E_1 volts and E_2 volts, respectively at 25°C. The pK_a values of acetic acid is (E_1 and E_2 are oxidation potentials)

(A) $\dfrac{E_1 + E_2}{0.118}$ (B) $\dfrac{E_2 - E_1}{0.118}$

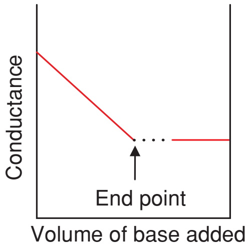
(C) $-\dfrac{E_1 + E_2}{0.118}$ (D) $\dfrac{E_1 - E_2}{0.118}$

13. Conductance measurements can be used to detect the end point of acid-base titrations. Which of the following plots correctly represent the end point of the titration of strong acid and strong base?

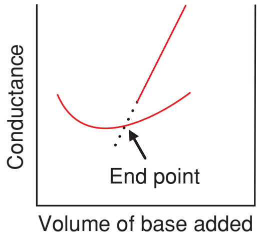
(A)



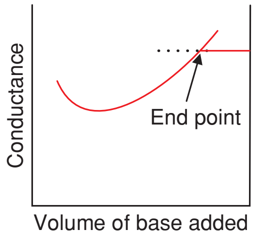
(B)



(C)



(D)



14. Equivalent conductance of 0.1 M HA (weak acid) solution is 10 S cm^2 equivalent^{-1} and that at infinite dilution is 200 S cm^2 equivalent^{-1}. Hence, pH of HA solution is

(A) 1.3 (B) 1.7
(C) 2.3 (D) 3.7

15. If x is the specific resistance of the electrolyte solution and y is the molarity of the solution, then λ_m is given by

(A) $\frac{1000x}{y}$ (B) $\frac{1000y}{x}$
(C) $\frac{1000}{xy}$ (D) $\frac{xy}{100}$

16. The solubility of $[Co(NH_3)_4Cl_2]\ ClO_4$, if the $\lambda_{Co(NH_3)_4Cl_2^+} = 50$, $\lambda_{ClO_4^-} = 70$, and the measured resistance was 33.5 Ω in a cell with cell constant of 0.20, is

(A) 59.7 m mol L^{-1}
(B) 49.7 m mol L^{-1}
(C) 39.7 m mol L^{-1}
(D) 29.7 m mol L^{-1}

17. With t is taken in seconds and I is taken in Ampere, the variation of I follows the equation

$$t^2 + I^2 = 25$$

What amount of Ag will be electrodeposited with this current flowing in the interval 0-5 second? (Atomic mass Ag = 108)

(A) 22 mg (B) 66 mg
(C) 77 mg (D) 88 mg

18. During an electrolysis of conc. H_2SO_4, perdisulphuric acid ($H_2S_2O_8$) and O_2 from in equimolar amount. The amount of H_2 that will form simultaneously will be
($2H_2SO_4 \rightarrow H_2S_2O_8 + 2H^+ + 2e^-$)

(A) thrice that of O_2 in moles.
(B) twice that of O_2 in moles.
(C) equal to that of O_2 in moles.
(D) half of that of O_2 in moles.

Multiple Correct Choice Type

19. On electrolysis of 10^{-6} M HCl solution

(A) O_2 gas is produced at the anode.
(B) Cl_2 is produced at the anode.
(C) O_2 gas is produced at the cathode.
(D) H_2 is produced at the cathode.

20. During discharge of lead storage battery, which of the following is/are true?

(A) Lead sulphate is formed.
(B) Lead is formed.
(C) H_2SO_4 is consumed.
(D) H_2SO_4 is formed.

21. On electrolysis, in which of the following, O_2 would be liberated at the anode?

(A) Dilute H_2SO_4 with Pt electrodes.
(B) Aqueous $AgNO_3$ solution with Pt electrodes.
(C) Dilute H_2SO_4 with Cu electrodes.
(D) Fused NaOH with Fe cathode and Ni anode.

22. If the same quantity of electricity is passed through three electrolytic cells containing $FeSO_4$, $Fe_2(SO_4)_3$ and $Fe(NO_3)_3$, then

(A) the amount of iron deposited in $FeSO_4$ and $Fe_2(SO_4)_3$ are equal.
(B) the amount of iron deposited in $FeSO_4$ is 1.5 times of the amount of iron deposited in $Fe(NO_3)_3$.
(C) the amount of iron deposited in $Fe_2(SO_4)_3$ and $Fe(NO_3)_3$ are equal.
(D) the same amount of gas is evolved in all three cases at the anode.

23. Which one is/are correct among the following? Given, the half-cell EMF's $E^o_{Cu^{2+}/Cu} = 0.337$, $E^o_{Cu^+/Cu} = 0.521$

(A) Cu^+ disproportionates.
(B) Cu and Cu^{2+} comproportionates (reverse of disproportionates) into Cu^+.
(C) $E^o_{Cu^{2+}/Cu} + E^o_{Cu^+/Cu}$ is positive.
(D) All of these.

24. Indicate the correct statements.

(A) Conductivity cells have cell constant values independent of the solution filled into the cell.
(B) DC (direct current) is not used for measuring the resistance of a solution.

(C) Kohlrausch law is valid both for strong and weak electrolytes.
(D) The constant k decreases but λ_M and λ_E increase on dilution.

Assertion-Reasoning Type

Choose the correct option from the following:

(A) Statement 1 and Statement 2 are True, Statement 2 is the correct explanation of the Statement 1.
(B) Statement 1 and Statement 2 are True, Statement 2 is NOT a correct explanation of the Statement 1.
(C) Statement 1 is True, Statement 2 is False.
(D) Statement 1 is False, Statement 2 is True.

25. Statement 1: The cell constant of a cell depends upon the nature of the material of the electrodes.
Statement 2: The observed conductance of a solution depends upon the nature of the material of the electrodes.

26. Statement 1: Gold chloride ($AuCl_3$) solution cannot be stored in a vessel made of copper, iron, nickel chromium, zinc or tin.
Statement 2: Gold is a very precious metal.

27. Statement 1: Molar conductivity of a weak electrolyte at infinite dilution cannot be determined experimentally.
Statement 2: Kohlrausch's law helps to find the molar conductivity of a weak electrolyte at infinite dilution.

28. Statement 1: On increasing dilution, the specific conductance keeps on increasing.
Statement 2: On increasing dilution, degree of ionization of weak electrolyte increase and mobility of ions also increase.

29. Statement 1: For the reaction: $Ni^{2+} + 2e^- \longrightarrow Ni$

$$Fe^{2+} + 2e^- \longrightarrow Fe$$

$$E^o_{Fe^{2+}/Fe} < E^o_{Ni^{2+}/Ni} \text{ and } E^o_{red} > 0$$

So Fe electrode is cathode and and Ni electrode is anode.
Statement 2: Because $\Delta G^\circ < 0$ and $E^o_{cell} > 0$, so cell is possible.

Comprehension Type

Paragraph I

If an element can exist in several oxidation states, it is convenient to display the reduction potentials corresponding to the various half reactions in diagrammatic form, known as Latimer diagram. The Latimer diagram for chlorine in acid solution is

$$ClO_4^- \xrightarrow{+1.20\text{ V}} ClO_3^- \xrightarrow{+1.18\text{ V}} HClO_2 \xrightarrow{+1.60\text{ V}}$$
$$HClO \xrightarrow{1.67\text{ V}} Cl_2 \xrightarrow{1.36\text{ V}} Cl^-$$

In basic solution it is

$$ClO_4^- \xrightarrow{0.37\text{ V}} ClO_3^- \xrightarrow{0.30\text{ V}} ClO_2^- \xrightarrow{0.68\text{ V}} ClO^-$$
$$\xrightarrow{0.42\text{ V}} Cl_2 \xrightarrow{1.36\text{ V}} Cl^-$$

The standard potentials for two non-adjacent species can also be calculated by using the concept that ΔG^o as an additive property but potential is not an additive property and $\Delta G^o = -nFE^o$. If a given oxidation state is a stronger oxidizing agent than in the next higher oxidation state, disproportionation can occur. The reverse of disproportionation is called comproportionation. The relative stabilities of the oxidation state can also be understood by drawing a graph of $\Delta G^o/F$ against oxidation state, known as Frost diagram, choosing the stability of zero oxidation state arbitrarily as zero. The most stable oxidation state of a species lies lowest in the diagram. Disproportionation is spontaneous if the species lies above a straight line joining its two product species.

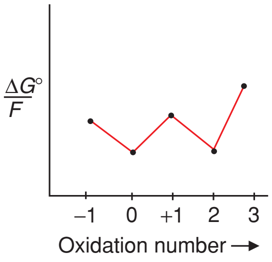
30. What is the potential of couple $\dfrac{ClO^-}{Cl^-}$ at pH = 14?

(A) 1.78 V (B) –0.94 V
(C) 0.89 V (D) –0.89 V

31. Which of the following statement is correct?

(A) Cl_2 undergoes disproportionation into Cl^- and ClO^- both at pH = 0 and pH = 14.
(B) Cl_2 undergoes disproportionation into Cl^- and ClO^- at pH = 14 but not at pH = 0.
(C) Cl_2 undergoes disproportionation into Cl^- and ClO^- at pH = 0 but not at pH = 14.
(D) None of these.

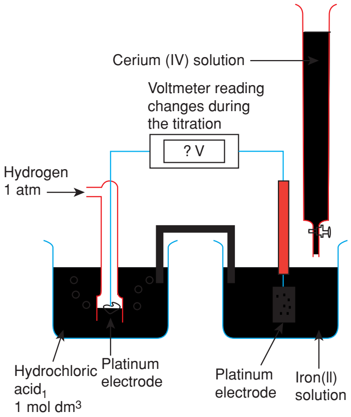
32. For a hypothetical element, the Frost diagram is shown in the following figure. Which of the following oxidation state is the least stable?



(A) –1 (B) 0
(C) +2 (D) +3

Paragraph II

Titrations are one of the methods we can use to discover the precise concentrations of solution. A typical titration involves adding a solution from a burette to another solution in a flask. The end point of the titration is found by watching a color change taking place. However, a problem arises when a suitable indicator cannot be found, or when the color changes involved are unclear. In cases redox potential may sometimes come to the rescue.

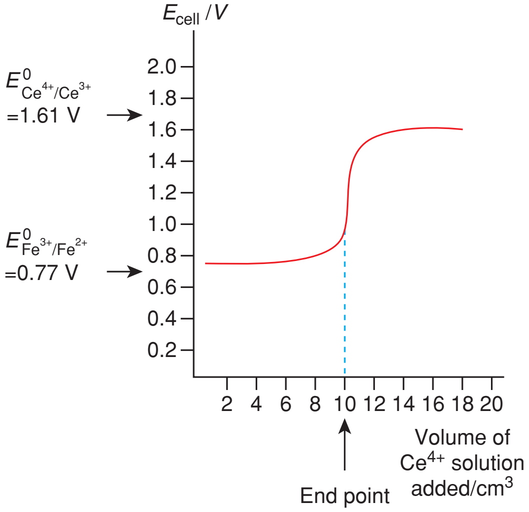


A particularly well known example (shown in the above figure) is a method of discovering the concentration of iron in a solution by titrating them with a solution of cerium (IV). The redox potential that are of interest here are $E^{\circ}_{Fe^{3+}/Fe^{2+}} = +0.77$ V and $E^{\circ}_{Ce^{4+}/Ce^{3+}} = +1.61$ V. These tell us that cerium (IV) ions are the oxidizing agents, and iron (II) ions are the reducing agent. They should react according to the equation

$$Fe^{2+}\,(aq) + Ce^{4+}\,(aq) \rightarrow Fe^{3+}\,(aq) + Ce^{3+}\,(aq)$$

Now imagine that we know the concentration of the cerium (IV) ions solution in the burette. We want to measure the concentration of the iron (II) solution. If we add just one drop of the cerium (IV) solution from the burette, some of the iron (II) ions will be oxidized. As a consequence the beaker would now contain not only a large number of unreacted ions, but also some iron (III) ions as well as cerium (III). The solution in the beaker now represents an iron (III)/iron (II) half-cell, although not at standard conditions. Thus the EMF of the cell will be near, but not equal, to $E^{\circ}_{Fe^{3+}/Fe^{2+}}$.

If we continue to add cerium (IV) solution, the number of iron (II) ions is gradually reduced and eventually only a very few are left (see Table). At this stage the next few drops of cerium (IV) solution convert all the remaining iron (II) ions into iron (III), and some of the cerium (IV) ions are left unreacted. Once this happens, we no longer have Fe(II) ions and a smaller number of cerium (IV) ions. The solution in the beaker now behaves as a cerium (IV)/cerium (III) half-cell (although not a standard one).



Just before all the iron (II) ions are converted into iron (III) we have a cell with an EMF of around +0.77 V. After all the iron (II) ions are oxidized, we have a cell with an EMF of about +1.61 V. This rapid rise in EMF occurs with the addition of just one drop of cerium (IV) solution. You should be able to understand why a graph of cell EMF against volume of cerium (IV) solution added looks like that of above figure. The end point of the titration can be read from the graph and the concentration of the iron (II) solution calculated in the usual way.

	Ions present				Cell	EMF/V
	Fe^{2+}	Fe^{3+}	Ce^{3+}	Ce^{4+}		
After the first few drops of Ce^{4+} (aq)	Many	Some	Some	None	Fe^{3-}/Fe^{2+}	A little less than 0.77
Near the end point	Some	Many	Many	None	Fe^{3+}/Fe^{2+}	A little more than 0.77
Just after end point	None	Many	Many	Some	Fe^{4+}/Fe^{3+}	A little more than 1.61

33. When an ion is converted into a complex ion, the redox potential changes. You can see this in the case of the EMF of the iron (III)/iron (II) system (+0.77 V) and the hexacyanoferrate (III)/hexacyanoferrate (II) system (+0.36 V). The cyanide ion is said to stabilize the oxidation state of the iron. If you were to make up a cell

$$\mathrm{Pt(s)}\left|\begin{array}{l}\mathrm{Fe(CN)_6^{3-}(aq), Fe(CN)_6^{4-}(aq),}\\ 1\,\mathrm{mol\,dm^{-3}}\end{array}\right\|\begin{array}{l}\mathrm{Fe^{3+}(aq), Fe^{2+}(aq)}\\ 1\,\mathrm{mol\,dm^{-3}}\end{array}\Bigg|$$

$$\mathrm{Pt(s)}$$

What would be the EMF and what would be the cell reaction?

(A) 0.41V, $[\mathrm{Fe(CN)_6}]^{4-}(\mathrm{aq}) + \mathrm{Fe^{3+}(aq)} \rightarrow [\mathrm{Fe(CN)_6}]^{3-}(\mathrm{aq}) + \mathrm{Fe^{2+}(aq)}$

(B) 0.13V, $[\mathrm{Fe(CN)_6}]^{4-}(\mathrm{aq}) + \mathrm{Fe^{3+}(aq)} \rightarrow [\mathrm{Fe(CN)_6}]^{3-}(\mathrm{aq}) + \mathrm{Fe^{2+}(aq)}$

(C) 0.41V, $[\mathrm{Fe(CN)_6}]^{3-}(\mathrm{aq}) + \mathrm{Fe^{2+}(aq)} \rightarrow [\mathrm{Fe(CN)_6}]^{4-}(\mathrm{aq}) + \mathrm{Fe^{3+}(aq)}$

(D) 0.13V, $[\mathrm{Fe(CN)_6}]^{3-}(\mathrm{aq}) + \mathrm{Fe^{2+}(aq)} \rightarrow [\mathrm{Fe(CN)_6}]^{4-}(\mathrm{aq}) + \mathrm{Fe^{3+}(aq)}$

34. The cell shown below was set up

$$\mathrm{Pt(s)}\left|\begin{array}{l}\mathrm{Fe^{3+}(aq), Fe^{2+}(aq),}\\ 1\,\mathrm{mol\,dm^{-3}}\end{array}\right\|\begin{array}{l}\mathrm{Br(aq), Br_2(l)}\\ 1\,\mathrm{mol\,dm^{-3}}\end{array}\Bigg|\mathrm{Pt(s)}$$

What would be the cell EMF? If potassium cyanide solution were added to the left hand half cell, what would you expect to happen to the EMF of the cell? $E^{\circ}_{\mathrm{Br_2/Br_2^-}} = 1.07\ \mathrm{V}$ and use data of previous question, if required.

(A) 0.30 V, EMF will increase from 0.30 V to 0.41 V.

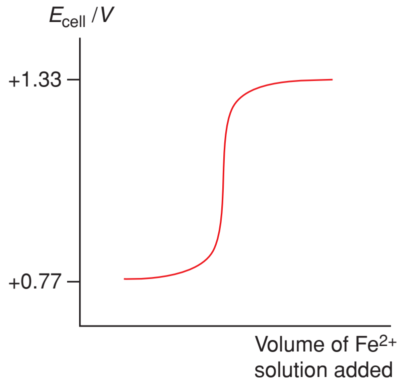
(B) 1.84 V, EMF will decrease from 1.84 V to 1.43 V.

(C) 0.30 V, EMF will increase from 0.30 V to 0.71 V.

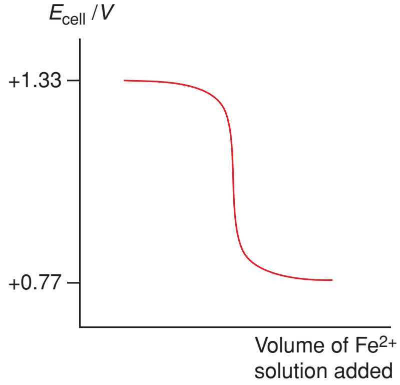
(D) 0.30 V, EMF will increase from 0.30 V to 0.43 V.

35. Imagine you were given a solution of potassium dichromate (VI) in a beaker, and a solution of iron (II) sulphate in a burette. You do not know the concentration of dichromate (VI) ions, but the concentration of the iron (II) solution is known. Your task is to carry out a redox titration using the two solutions in order to determine the concentration of dichromate (VI) ions. Sketch a graph how the EMF changes in the course of above titration. $E^{\circ}_{\mathrm{Cr_2O_7^{2-}/Cr^{3+}}} = 1.33\ \mathrm{V}$, $E^{\circ}_{\mathrm{Fe^{3+}/Fe^{2+}}} = 0.77\ \mathrm{V}$.

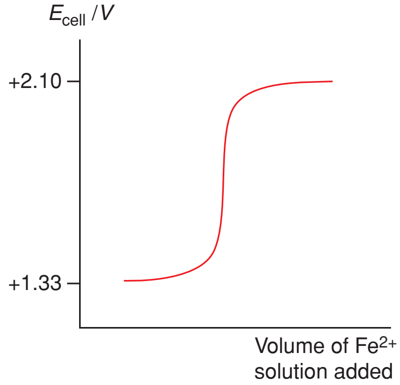
(A)



(B)



(C)



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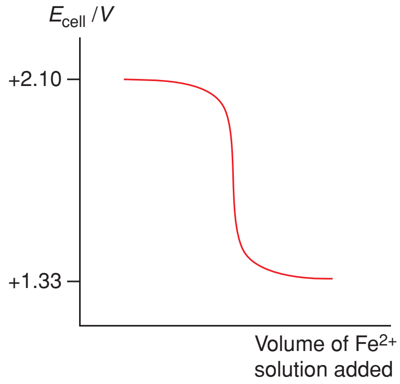


Matrix-Match Type

36. Match the quantities with the factors on which they depend.

Column I	Column II
(A) Molar conductance	(p) Temperature
(B) Electrode potential	(q) Concentration of species involved
(C) Standard electrode potential	(r) Nature of substance involved
(D) EMF of a cell in operation	(s) Stoichiometric coefficient of the reaction

37. Assume inert electrolyte used in salt bridge in all the given cells is KCl. (K_a of HCOOH = 2×10^{-4}). Then match the cell reaction with the observation.

Column I	Column II
(A) $Zn \mid ZnSO_4 (1M) \| ZnSO_4 (2M) \mid Zn$	(p) Spontaneous cell reaction
(B) $Cu \mid CuCl_2 (1M) \mid CuSO_4 (2M) \mid Cu$	(q) Osmotic pressure of cathodic solution is greater than that of anodic solution
(C) $Ag \mid AgCl$ (sat. sol.)$\| AgNO3(1M) \mid Ag$	(r) At equilibrium condition of the cell, freezing point of anodic solution is higher than of cathodic solution
(D) $Pt \mid H_2 \mid$ HCOOH (1M)$\|$HCl (1M)$\mid H_2 \mid Pt$	(s) At equilibrium condition of the cell, boiling point of cathodic solution is higher than that of anodic solution

38. Match the electrolytic solution and the electrode with the observation.

Column I	Column II
(A) Molten $PbCl_2$ using inert electrode	(p) Metal of salt will reduced.
(B) Sodium chloride solution using inert electrode	(q) $H_2O + 2e^- \rightarrow H_2(g) + 2OH^-$
(C) Silver nitrate solution with silver electrode	(r) Solution becomes basic after electrolysis
(D) Sodium nitrate solution using inert electrode	(s) Solution becomes acidic after electrolysis

CHEMICAL KINETICS

Single Correct Choice Type

1. For a gas reaction at T(K) the rate is given by $\frac{dp_A}{dt} = k'p_A^2 \text{ atm h}^{-1}$. If the rate equation is expressed as $-r_A = -\frac{1}{V}\frac{dn_A}{dt} = kC_A^2 \text{ mol L}^{-1}\text{ h}^{-1}$, the rate constant k is given by

(A) $k = k'$ (B) $k = k'\ RT$

(C) $k = k'/RT$ (D) $k = k'\ (RT)^2$

where R is gas constant in cal g^{-1} mol^{-1} K^{-1}

2. In the following reaction: $x_A \longrightarrow y_B$

$$\log\left[-\frac{d[A]}{dt}\right] = \log\left[\frac{d[B]}{dt}\right] + 0.3$$

where –ve sign indicates rate of disappearance of the reactant. Thus, $x : y$ is

(A) 1 : 2 (B) 2 : 1

(C) 3 : 1 (D) 3 : 10

3. Two substances A ($t_{1/2}$ = 5 min) and B ($t_{1/2}$ = 15 min) are taken in such a way that initially [A] = 4[B]. The time after which both the concentration will be equal is (assuming reactions are of first order)

(A) 5 min.

(B) 15 min.

(C) 20 min.

(D) Concentration can never be equal.

4. The kinetic of hydrolysis of methyl acetate in excess dilute HCl at 25ºC was followed by withdrawing 2 mL of the reaction mixture at intervals of (t), adding 50 mL water and titrating with baryta water. Determine the velocity constant of hydrolysis.

t (in minute)	0	75	119	259	∞
Titer value (in mL)	19.24	24.20	26.60	32.23	42.03

$$\left[\ln\frac{22.79}{17.83} = 0.2454, \ln\frac{22.79}{15.43}\ 0.39, \ln\frac{22.79}{9.8} = 0.8439\right]$$

(A) 3.27×10^{-3} min^{-1}

(B) 3.27×10^{-3} s^{-1}

(C) 1.5×10^{-3} min^{-1}

(D) 1.5×10^{-3} s^{-1}

5. For a reaction, A → B + C, it was found that at the end of 10 min from the start, the total optical rotation of the system was 50° and when the reaction is complete, it was 100°. Assuming that only B and C are optically active and dextrorotatory, calculate the rate constant of this first order reaction,

(A) $k = 0.695\ \text{min}^{-1}$ (B) $k = 0.0693\ \text{s}^{-1}$
(C) $k = -0.0693\ \text{min}^{-1}$ (D) $k = 0.00693\ \text{s}^{-1}$

6. The decomposition of hydrogen peroxide in an aqueous solution is a reaction of first order. It can be followed by titrating 10 mL portions of reaction mixture at various times from the beginning of reaction against a standard solution of $KMnO_4$. Volume of $KMnO_4$ solution used in each case is proportional to the remaining concentration of H_2O_2. From the following data, calculate the rate constant of the reaction.

Time (in second)	0	600	1200
$KMnO_4$ sol. used (in mL)	22.8	13.8	8.20

(A) $k = 8.44 \times 10^{-4}\ \text{s}^{-1}$
(B) $k = 8.44 \times 10^{-2}\ \text{s}^{-1}$
(C) $k = 2.44 \times 10^{-6}\ \text{s}^{-1}$
(D) $k = 2.22 \times 10^{-4}\ \text{s}^{-1}$

7. For the consecutive unimolecular type first-order reaction $A \xrightarrow{k_1} R \xrightarrow{k_2} S$, the concentration of component R, C_R at any time t is given by

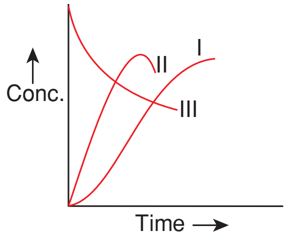
$$C_R = C_{A_0} \cdot K_1 \left[\frac{e^{-k_1 t}}{(k_2 - k_1)} + \frac{e^{-k_2 t}}{(k_1 - k_2)} \right]$$

if $C_A = C_{A_0}$, $C_R = C_{R_0} = 0$ at $t = 0$, the time at which the maximum concentration of R occurs is

(A) $t_{\max} = \dfrac{k_2 - k_1}{\ln(k_2/k_1)}$ (B) $t_{\max} = \dfrac{\ln(k_2/k_1)}{k_2 - k_1}$

(C) $t_{\max} = \dfrac{e^{k_2/k_1}}{k_2 - k_1}$ (D) $t_{\max} = \dfrac{e^{k_2 - k_1}}{k_2 - k_1}$

8. A first order homogeneous reaction of the type X → Y → Z (consecutive reaction) is carried out in a continous stirred-tank reactor. Which of the following curves respectively show the variation of the concentration of X, Y and Z with time?



(A) I, II, III (B) III, II, I
(C) III, I, II (D) II, III, I

9. For the consecutive unimolecular type first order reaction $A \xrightarrow{k_1} R \xrightarrow{k_2} S$, the concentration of component A, C_A at any time t is given by

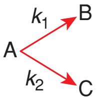
(A) $C_A = C_{A_0} e^{(k_1 + k_2)t}$

(B) $C_A = C_{A_0} e^{-(k_1 + k_2)t}$

(C) $C_A = C_{A_0} e^{-k_1 t}$

(D) $C_A = C_{A_0} e^{k_1 t}$

10. A substance undergoes first order decomposition. The decomposition follows two parallel first order reactions as



$k_1 = 1.26 \times 10^{-4}\ \text{s}^{-1}$ and
$k_2 = 3.8 \times 10^{-5}\ \text{s}^{-2}$

The percentage distributions of B and C are

(A) 80% B and 20% C
(B) 76.83% B and 23.17% C
(C) 90% B and 10% C
(D) 60% B and 40% C

11. The reaction, X + 2Y + Z → N occurs by the following mechanism

(i) $X + Y \rightleftharpoons M$ (very rapid equilibrium)
(ii) M + Z → O (slow)
(iii) O + Y → N (very fast)

What is the rate law for this reaction?

(A) Rate = k[Z]
(B) Rate = $k[X][Y]^2[Z]$
(C) Rate = k[N]
(D) Rate = k [X] [Y] [Z]

12. The reaction of hydrogen, and iodine monochloride is represented by the equation:

$$H_2(g) + 2ICl(g) \rightarrow 2HCl(g) + I_2(g)$$

This reaction is first order in $H_2(g)$ and also first order in ICl(g). Which of these proposed mechanisms can be consistent with the given information about this reaction?

Mechanism I: $H_2(g) + 2ICl(g) \rightarrow 2HCl(g) + I_2(g)$

Mechanism II:
$H_2(g) + ICl(g) \xrightarrow{\text{Slow}} HCl(g) + HI(g)$

$$HI(g) + ICl(g) \xrightarrow{\text{fast}} HCl(g) + I_2(g)$$

(A) I only (B) II only
(C) both I and II (D) neither I nor II

13. For a certain reaction of order n, the time for half change, $t_{1/2}$, is given by $t_{1/2} = \frac{[2-\sqrt{2}]}{k} \times C_0^{1/2}$ where k is the rate constant and C_0 is the initial concentration. What is n?

(A) 1 (B) 2
(C) 0 (D) 0.5

14. In the Lindemann theory of unimolecular reactions, it is shown that the apparent rate constant for such a reaction is $k_{\text{app}} = \frac{k_1 C}{1+\alpha C}$ where C is the concentration of the reactant, k_1 and α are constants. Calculate the value of C for which k_{app} has 90% of its limiting value at C tending to infinitely large values, given $\alpha = 9 \times 10^5$.

(A) 10^{-6} mol L^{-1} (B) 10^{-4} mol L^{-1}
(C) 10^{-5} mol L^{-1} (D) 5×10^{-5} mol L^{-1}

15. Given that for a reaction of order n, the integrated form of the rate equation is $k = \frac{1}{t(n-1)}\left[\frac{1}{C^{n-1}} - \frac{1}{C_0^{n-1}}\right]$ where C_0 and C are the values of the reactant concentration at the start and after time t. What is the relationship between $t_{3/4}$ and $t_{1/2}$ where $t_{3/4}$ is the time required for C to become 1/4 C_0?

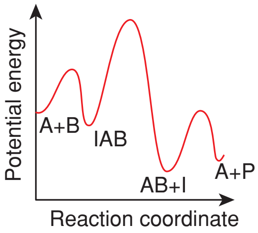
(A) $t_{3/4} = t_{1/2}\,[2^{n-1} + 1]$
(B) $t_{3/4} = t_{1/2}\,[2^{n-1} - 1]$
(C) $t_{3/4} = t_{1/2}\,[2^{n+1} - 1]$
(D) $t_{3/4} = t_{1/2}\,[2^{n+1} + 1]$

16. The following mechanism has been proposed for the exothermic catalyzed complex reaction.

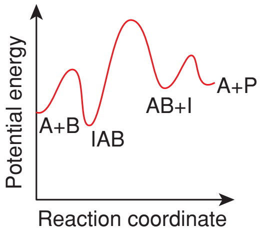
$$A + B \underset{}{\overset{\text{fast}}{\rightleftharpoons}} IAB \underset{\text{slow}}{\xrightarrow{k_1}} AB + I \underset{\text{fast}}{\xrightarrow{k_2}} P + A$$

If k_1 is much smaller than k_2. The most suitable qualitative plot of potential energy versus reaction coordinates for the above reaction.

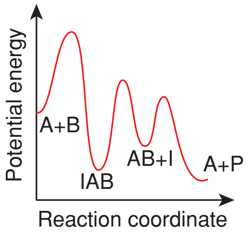
(A)



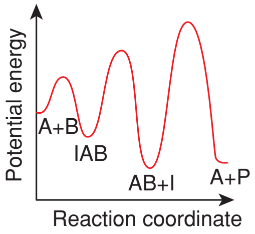
(B)



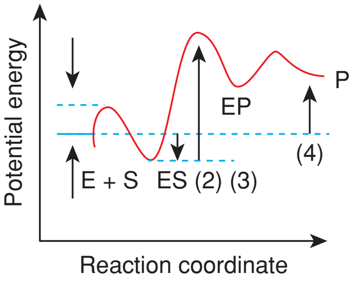
(C)



(D)



17. Choose the correct set of identification.



	(1)	(2)	(3)	(4)
(A)	ΔE for E+S→ES	E_a for ES→EP	$\Delta E_{\text{overall}}$ for S→P	E_a for EP→E+P
(B)	E_a for E+S→ES	ΔE for E+S→ES	E_a for ES→EP	$\Delta E_{\text{overall}}$ for S→P
(C)	E_a for ES→EP	E_a for EP→E+P	$\Delta E_{\text{overall}}$ for S→P	ΔE for EP→E+P
(D)	E_a for E+S→ES	E_a for ES→EP	E_a for EP→E+P	$\Delta E_{\text{overall}}$ for S→P

Multiple Correct Choice Type

18. Activation energy of a reaction depends on

(A) nature of reactants.
(B) temperature.
(C) conc. of reactants.
(D) presence of catalyst.

19. The rate law for the reaction,

$$\mathrm{RCl} + \mathrm{NaOH(aq)} \rightarrow \mathrm{ROH} + \mathrm{NaCl}$$

is given by rate = k[RCl]. The rate of the reaction will be

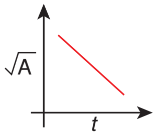
(A) doubled on doubling the concentration of sodium hydroxide.
(B) halved by reducing the concentration of alkyl halide to one-half.
(C) increased on increasing the temperature of the reaction.
(D) unaffected by increasing the temperature of the reaction.

20. For producing effective collisions, the colliding molecules must possess

(A) proper orientation.
(B) energy equal to activation energy.
(C) energy equal to or greater than threshold energy.
(D) energy greater than threshold energy.

21. For the reaction A→B, the rate law expression is $-\dfrac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = k[\mathrm{A}]^{1/2}$. If initial concentration of [A] is $[\mathrm{A}]_0$, then

(A) The integrated rate expression is $k = \dfrac{2}{t}\left(\mathrm{A}_0^{1/2} - \mathrm{A}^{1/2}\right)$.
(B) The graph of $\sqrt{\mathrm{A}}$ vs t will be



(C) The half-life period $t_{1/2} = \dfrac{k}{2[\mathrm{A}]_0^{1/2}}$.
(D) The time taken for 75% completion of reaction $t_{3/4} = \dfrac{\sqrt{[\mathrm{A}]_0}}{k}$.

Assertion-Reasoning Type

Choose the correct option from the following:

(A) Statement 1 and Statement 2 are True, Statement 2 is the correct explanation of the Statement 1.
(B) Statement 1 and Statement 2 are True, Statement 2 is NOT a correct explanation of the Statement 1.
(C) Statement 1 is True, Statement 2 is False.
(D) Statement 1 is False, Statement 2 is True.

22. **Statement 1:** For a first order reaction $t_{1/2}$ is independent of the initial concentration of reactants.
Statement 2: For a first order reaction $t_{1/2}$ is twice the $t_{3/4}$.

23. **Statement 1:** If initial concentration of all the reactants is in stoichiometric ratio their half-life is same irrespective of the order.
Statement 2: Molecularity of a complex reaction is not defined.

24. **Statement 1:** The time of completion of reactions of type $\mathrm{A} \rightarrow \mathrm{Product}$ (order < 1) may be determined.
Statement 2: Reactions with order ≥ 1 are either too slow or too fast and hence the time of completion cannot be determined.

25. **Statement 1:** A catalyst provides an alternative path to the reaction in which conversion of reactants into products takes place quickly.
Statement 2: The catalyst forms an activated complex of lower potential energy, with reactants by which more number of molecules is able to cross the barrier per unit of time.

Comprehension Type

Paragraph I

For the reaction, if effective rate constant K is given by: $K' = \dfrac{2K_2}{K_3}\left(\dfrac{K_1}{K_5}\right)^{1/5}$

26. The effective activation energy is

(A) $E'_{\mathrm{a}} = E_{\mathrm{a}2} - E_{\mathrm{a}3} + \dfrac{1}{5}E_{\mathrm{a}1} - \dfrac{1}{5}E_{\mathrm{a}5}$
(B) $E'_{\mathrm{a}} = E_{\mathrm{a}1} + E_{\mathrm{a}2} + E_{\mathrm{a}3} + E_{\mathrm{a}5}$
(C) $E'_{\mathrm{a}} = E_{\mathrm{a}1} + E_{\mathrm{a}2} - E_{\mathrm{a}3} - E_{\mathrm{a}5}$
(D) $E'_{\mathrm{a}} = E_{\mathrm{a}2} + E_{\mathrm{a}3} - E_{\mathrm{a}5} - E_{\mathrm{a}1}$

27. The effective frequency factor

(A) $A' = \dfrac{A_2}{A_3}\left(\dfrac{A_1}{A_5}\right)^2$
(B) $A' = 2\left(\dfrac{A_2}{A_3}\right)\left(\dfrac{A_1}{A_5}\right)^{1/5}$
(C) $A' = A_1 \times A_2 \times A_3 \times A_4$
(D) $A' = \left(\dfrac{A_1}{A_2}\right)\left(\dfrac{A_3}{A_5}\right)^{1/5}$

28. The rate constant for the reactions says that

(A) it is first order reaction.
(B) it is zero order reaction
(C) it is second order reaction
(D) it cannot be predicted by the data given.

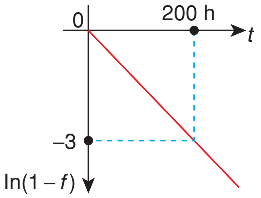
Paragraph II

Oxidation of metals is generally a slow electrochemical reaction involving many steps. These steps involve electron transfer reactions. A particular type of oxidation involve overall first order kinetics with respect to fraction of unoxidized metal $(1 - f)$ surface thickness relative to maximum thickness (T) of oxidized surface, when metal surface is exposed to air for considerable period of time.

Rate law: $\dfrac{df}{dt} = k(1-f)$

where $f = \dfrac{x}{T}$, x is thickness of oxide film at t and T is thickness of oxide film at $t = \infty$.

A graph of $\ln(1 - f)$ vs. t is shown in the following figure.



29. The time taken for thickness to grow 50% of T is

(A) 23.1 h (B) 46.2 h
(C) 100 h (D) 92.4 h

30. The exponential variation of f with $t(h)$ is given by

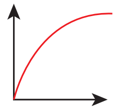
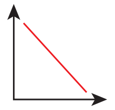
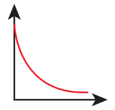
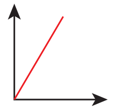
(A) $(1 - e^{-3t/200})$ (B) $e^{-3t/200} - 1$
(C) $e^{-3t/200}$ (D) $e^{3t/200}$

Matrix-Match Type

31. Match the reactions and their rate constants with the observation.

Column I	Column II
(A) $A + B \longrightarrow C + D$ $r = k_1[A][B]$	(p) Unit of rate constant possess concentration unit
(B) $A + B \rightarrow C + D$ $r = k_2[A][B]_0$	(q) Rate constant for the reaction of both the reactants are equal
(C) $A + B \rightarrow C + D$ $r = k_3[A]_0\,[B]_0$	(r) Rate of consumption of atleast one of the reactant is equal to rate of production of atleast one of the products
(D) $2A + B \rightarrow 2C + 3D$ $r = k_3[A]_0\,[B]_0$	(s) If both reactants are taken in stoichiometric ratio, half life for both reactants are equal

32. Match the relation with the corresponding plot.

Column I	Column II
(A) $\dfrac{d[B]}{dt}$ vs. $-\dfrac{d[A]}{dt}$	(p) 
(B) [A] vs. t for first order	(q) 
(C) [B] vs. t for first order	(r) 
(D) [A] vs. t for first order	(s) 

33. For the first consecutive reactions.

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

The reaction is started with some amount of A. Match the given observation with the time related with above reaction.

Column I	Column II
(A) Rate of formation of C is maximum	(p) At time $t = t_{1/2}$ of A (given $k_2 = 2k_1$)
(B) $[B]_t = [C]_t$	(q) At time $t = \dfrac{1}{k_2 - k_1}\ln\left(\dfrac{k_2}{k_1}\right)$
(C) $[A]_t = [B]_t$	(r) At time t when rate of formation of B is maximum
	(s) At time $t = \dfrac{\ln(2 - k_2/k_1)}{k_1 - k_2}$ and $k_1 > k_2$

SURFACE CHEMISTRY

Single Correct Choice Type

1. A colloidal solution is subjected to an electrical field. The particles move towards anode. The coagulation of the same sol is studied using NaCl, $BaCl_2$ and $AlCl_3$ solutions. Their coagulating power should be

(A) $NaCl > BaCl_2 > AlCl_3$
(B) $BaCl_2 > AlCl_3 > NaCl$
(C) $AlCl_3 > BaCl_2 > NaCl$
(D) $BaCl_2 > NaCl > AlCl_3$

2. On adding few drops of dil. HCl to freshly precipitated ferric hydroxide, a red colored colloidal solution is obtained. This phenomenon is known is

(A) peptization. (B) dialysis.
(C) protective action. (D) dissolution.

3. In the preparation of AgI sol, the excess of $AgNO_3$ is added to potassium iodide solution. The particles of the sol will acquire

(A) negative charge. (B) positive charge.
(C) no charge. (D) unpredictable.

4. Milk is a colloid in which

(A) a liquid is dispersed in liquid.
(B) a solid is dispersed in liquid.
(C) a gas dispersed in liquid.
(D) some sugar is dispersed in water.

5. Which of the following statement is not correct in respect of hydrophilic sol?

(A) The particles are hydrated.
(B) They are quite stable and are not easily coagulated.
(C) They are irreversible.
(D) There are considerable interactions between the dispersed phase and the dispersion medium.

6. Which of the following is the cause of Brownian movement of colloids?

(A) Thermal agitation in medium.
(B) Collision due to air molecules.
(C) Unbalanced impacts by molecules of the dispersion medium.
(D) Cause is unpredictable.

7. Tyndall effect in colloidal solution is due to

(A) scattering of light.
(B) reflection of light.
(C) absorption of light.
(D) presence of electrically charged particles.

8. When a graph is plotted between log x/m and log p, it is straight line with an angle 45° and intercept 0.3010 on y-axis. If initial pressure is 0.3 atm, what will be the amount of gas adsorbed per gram of adsorbent?

(A) 0.4 (B) 0.6
(C) 0.8 (D) 0.1

9. Finally divided catalyst has greater surface area and has greater catalytic activity than the compact solid. If a total surface area of 6291456 cm^2 is required for adsorption of gaseous reaction in a catalyzed reaction, then how many splits should be made of cube exactly 1 cm in length?

(A) 60 (B) 80
(C) 20 (D) 22

10. For the coagulation of 200 mL of As_2S_3 solution, 10 mL of 1 M NaCl is required. What is the coagulating value of NaCl?

(A) 200 (B) 100
(C) 50 (D) 25

11. At critical micelle concentration (CMC), the surfactant molecules

(A) decompose.
(B) become completely soluble.
(C) associate.
(D) dissociate.

Multiple Correct Choice Type

12. Which of the following colloidal solutions contain negatively charged colloidal particles?

(A) $Fe(OH)_3$ sol
(B) As_2S_3 sol
(C) Blood
(D) Gold. sol

13. Which of the following statements are true?

(A) Soap solution contains ionic micelles as the colloidal particles.
(B) A water in oil emulsion easily dissolves in water.
(C) Chemisorption is highly specific.
(D) Chemisorption occurs in the form of multimolecular layers.

14. A lyophobic colloidal solution can be precipitated by

(A) adding lyophilic colloid.
(B) heating.
(C) adding electrolyte.
(D) adding oppositely charged colloid.

15. When a negatively charged colloid like As_2S_3 sol is added to positively charged $Fe(OH)_3$ sol in suitable amounts

(A) both the sols are precipitated simultaneously.
(B) this process is called mutual coagulation.
(C) they becomes positively charged colloids.
(D) they becomes negatively charged colloids.

16. The origin of charge on colloidal solution is

(A) self-dissociation.
(B) electron capture during Bredig's arc method.

(C) selective adsorption of ion on their surface.
(D) it is due to addition of protective colloids.

17. Which of the following are correct statements?

(A) Spontaneous adsorption of gases on solid surface is an exothermic process as entropy decreases during adsorption.
(B) Formation of micelles takes place when temperature is below Kraft temperature (T_k) and concentration is above critical micelle concentration.
(C) A colloid of $Fe(OH)_3$ is prepared by adding NaOH in $FeCl_3$ solution, the particles of this sol will more towards cathode during electrophoresis.
(D) According to Hardy-Schulze rule the coagulation (flocculating) value of Fe^{3+} ion will be more than Ba^{2+} or Na^+.

18. Which of the following are incorrect statements?

(A) Hardy-Schulze rule is related to coagulation.
(B) Brownian movement and Tyndall effect are the characteristic of colloids.
(C) In gel, the liquid is dispersed in liquid.
(D) Lower the gold number more is the protective power of lyophilic sols.

Assertion-Reasoning Type

Choose the correct option from the following:

(A) Statement 1 and Statement 2 are True, Statement 2 is the correct explanation of the Statement 1.
(B) Statement 1 and Statement 2 are True, Statement 2 is NOT a correct explanation of the Statement 1.
(C) Statement 1 is True, Statement 2 is False.
(D) Statement 1 is False, Statement 2 is True.

19. Statement 1: True solutions do not exhibit Tyndall effect.
Statement 2: In true solutions, the size of solute particles is small.

20. Statement 1: Lyophilic colloids are generally stable.
Statement 2: In lyophilic colloids there is great affinity between disperse phase and dispersion medium.

21. Statement 1: For the adsorption of a gas on a solid, the plot of log x/m versus log p is linear with slope equal to $1/n$.
Statement 2: According to Freundlich adsorption isotherm $\frac{x}{m} = kp^{1/n}$.

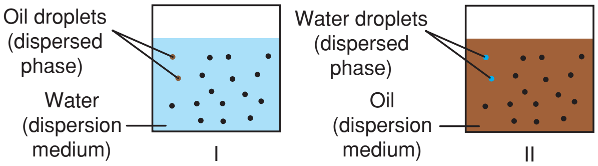
Comprehension Type

Paragraph I

If a pair of immiscible liquids such as olive oil and water are mixed and shaken vigorously, a dispersion of very fine droplets of one liquid in the other will result. Such dispersion is termed emulsion.

(i) One of the components in emulsion is water and the other one an oily substance immiscible in water.
(ii) Emulsion droplets are bigger than sol particles (10^{-6} m) and can be seen under an ordinary microscope or sometimes even with a magnifying glass.
(iii) Emulsions resemble lyophobic sols in some of the properties.
(iv) Emulsion can be identified by dye-test.

22. In the following emulsion


Oil droplets (dispersed phase)
Water (dispersion medium)
I
Water droplets (dispersed phase)
Oil (dispersion medium)
II

(A) I is of oil-in-water type and II is of water-in-oil type.
(B) I is of water-in-oil type and II is of oil-in-water type.
(C) both are of oil-in-water type.
(D) both are of water-in-oil type.

23. An oil-soluble dye is shaken with the given emulsion under study. We observe that whole background appears colored. This indicates that emulsion is

(A) water-in-oil type.
(B) oil-in-water type.
(C) liquid under study is pure oil.
(D) liquid under study is pure water.

24. An oil-soluble dye is shaken with the given emulsion under study. We observe coloured drops when seen under microscope. Thus emulsion is

(A) water-in-oil type.
(B) oil-in-water type.
(C) liquid under study is pure oil.
(D) liquid under study is pure water.

Paragraph II

The cloud consists of charged particles of water dispersed in air. Some of them are positively charged, others are negatively charged. When positively charged clouds come closer they cause lightening and thundering whereas when positive and negative charged colloids come closer, they cause heavy rain by aggregation of minute particles. It is possible to cause artificial rain by throwing electrified sand or silver iodide from an aeroplane and thus coagulating the mist hanging in air. Smoke screen is a cloud of smoke used to hide military, naval police, etc. It consists of fine particles of TiO_2.

25. When excess of $AgNO_3$ is treated with KI solution, AgI forms

(A) positive charged sol.
(B) negatively charged sol.
(C) neutral sol.
(D) true solution.

26. AgI helps in artificial rain because

(A) it helps in ionization of water.
(B) it helps in dispersion process.
(C) it helps in coagulation.
(D) All of the above.

27. Smoke screens consist of

(A) fine particles of TiO_2 dispersed in air by aeroplanes.
(B) fine particles of AgI dispersed in air by aeroplanes.
(C) fine particles of Al_2O_3 dispersed in air by aeroplaenes.
(D) none of these.

Matrix-Match Type

28.

Column I	Column II
(A) Gold sol	(p) Bredig's arc method
(B) Purification of colloidal solution	(q) Negatively charged
(C) As_2S_3 sol	(r) Ultra-centrifugation
(D) Zeta potential	(s) Electro kinetic potential
(E) Casein	(t) Double decomposition reaction
	(u) Protective colloid

29. Match the properties of colloidal solutions with their applications.

Column I	Column II
(A) Tyndall effect	(p) Zig-zag motion
(B) Brownian movement	(q) Sky is blue
(C) Electrophoresis	(r) Coagulation of colloids
(D) Hardy-Schulz rule	(s) Charge on colloidal solution
(E) Froth floatation	(t) Emulsion of pine oil
	(u) Gold number

NUCLEAR CHEMISTRY

Single Correct Choice Type

1. 1 mol of α emitting nuclide ${}^{A}_{z}X$ ($t_{1/2} = 10$ h) was placed in a sealed container. The time required for the accumulation of 4.52×10^{23} helium atoms in the container is

(A) 4.52 h (B) 9.40 h
(C) 10.0 h (D) 20.0 h

2. Which of the following is (n, p) type reaction?

(A) ${}^{13}_{5}C + {}^{1}_{1}H \rightarrow {}^{14}_{6}C$
(B) ${}^{14}_{7}N + {}^{1}_{1}H \rightarrow {}^{15}_{8}O$
(C) ${}^{27}_{13}Al + {}^{1}_{0}n \rightarrow {}^{27}_{12}Mg + {}^{1}_{1}H$
(D) ${}^{235}_{92}U + {}^{1}_{0}n \rightarrow {}^{140}_{54}Xe + {}^{94}_{88}Sr$

3. The activity of radioactive nuclide (X^{100}) is 6.023 Curie. If its disintegration constant is $3.7 \times 10^4\ s^{-1}$, the mass of X is

(A) 10^{-3} g (B) 10^{-15} g
(C) 10^{-6} g (D) 10^{-14} g

4. Review the nuclear reaction:

$$ {}^{226}_{88}Ra \xrightarrow{-\alpha} Rn \xrightarrow{-\alpha} Po \xrightarrow{-\alpha} Pb \xrightarrow{-\beta} Bi $$

Point out the correct statement.

(A) Ra, Rn, Po, Pb (isodiapheres), Pb and Bi (isobars).
(B) Ra, Rn (isotopes) Po, Pb, Bi (isobars).
(C) Rn, Po, Pb (isotopes) Ra, Pb, Bi (isobars).
(D) None of these.

5. ${}^{27}_{13}Al$ is a stable isotope. ${}^{29}_{13}Al$ is expected to disintegrated by

(A) α emission.
(B) ${}^{0}_{-1}\beta$ emission.
(C) positron emission.
(D) proton emission.

6. Two radioactive material A_1 and A_2 have decay constants of $10\lambda_0$ and λ_0. If initially they have same number of nuclei, then after time $1/9\lambda_0$ the ratio of number of their undecayed nuclei will be

(A) $\frac{1}{e}$ (B) $\frac{1}{e^2}$
(C) $\frac{1}{e^3}$ (D) $\frac{\sqrt{e}}{1}$

7. Consider the following nuclear reactions:

$$^{238}_{92}\text{M} \rightarrow {}^{X}_{Y}\text{N} + 2\,{}^{4}_{2}\text{He};\quad {}^{X}_{Y}\text{N} \rightarrow {}^{A}_{B}\text{L} + 2\beta^{+}$$

The number of neutrons in the element L is

(A) 142 (B) 144
(C) 140 (D) 146

8. Helium nuclei combine to form an oxygen nucleus. The energy released per nucleon of oxygen nucleus is (Given: $m_0 = 15.834$ amu and $m_{\text{He}} = 4.0026$ amu)

(A) 10.24 MeV. (B) 0 MeV.
(C) 5.27 MeV. (D) 4 MeV.

9. A radioactive element gets spilled over the floor of a room. Its half-life period is 30 days. If the initial activity is ten times the permissible value, after how many days will it be safe to enter the room?

(A) 1000 days (B) 300 days
(C) 10 days (D) 100 days

10. Read the following statements and assign as True (T) and False (F):

(i) The half-life period of a radioactive element X is same as the mean-life time of another radioactive element Y. Initially both of them have the same number of atoms. Then Y will decay at a faster rate than X.
(ii) The electron emitted in beta radiation originates from decay of a neutron in a nucleus.
(iii) The half-life of ^{215}At is 100 ms. The time taken for the radioactivity of a sample of ^{215}At to decay to 1/16th of its initial value is 400 ms.
(iv) The volume (V) and mass (m) of a nucleus are related as $V \propto m$.
(v) Given a sample of radius 226 having half-life of 4 days. The probability of nucleus disintegration within 2 half-lives is 3/4.

Select the correct code for above.

(A) TTTTT (B) TFTTF
(C) FTFTF (D) FTTTF

11. The analysis of a mineral of uranium reveals that ratio of mole of ^{206}Pb and ^{238}U in sample is 0.2. If effective decay constant of process $^{238}\text{U} \rightarrow {}^{206}\text{Pb}$ is λ, then age of rock is

(A) $\frac{1}{\lambda}\ln\frac{5}{4}$ (B) $\frac{1}{\lambda}\ln\left(\frac{5}{1}\right)$
(C) $\frac{1}{\lambda}\ln\frac{4}{1}$ (D) $\frac{1}{\lambda}\ln\left(\frac{6}{5}\right)$

12. The half-life of ^{99}Tc is 6.0 h. The delivery of a sample of ^{99}Tc from the reactor to the nuclear medicine lab of a certain hospital takes 3.0 h. What is the minimum amount of ^{99}Tc that must be shipped in order for the lab to receive 10.0 mg?

(A) 20.0 mg (B) 15.0 mg
(C) 14.1 mg (D) 12.5 mg

13. The average (mean) life at a radio nuclide which decays by parallel path is

$$\text{A} \xrightarrow{\lambda_1} \text{B};\qquad \lambda_1 = 1.8 \times 10^{-2}\ \text{s}^{-1}$$
$$2\text{A} \xrightarrow{\lambda_2} \text{C};\qquad \lambda_2 = 10^{-3}\ \text{s}^{-1}$$

(A) 52.63 s (B) 500 s
(C) 50 s (D) None

14. The radioactivity of a sample is R_1 at a time t_1 and R_2 at a time t_2. If the half-life of the specimen is t, the number of atoms that have disintegrated in the time $(t_2 - t_1)$ is equal to

(A) $(R_1t_1 - R_2t_2)$ (B) $(R_1 - R_2)$
(C) $(R_1 - R_2)/t$ (D) $(R_1 - R_2)t/0.693$

Multiple Correct Choice Type

15. A stable nuclide, in general, may have

(A) even number of protons and even number of neutrons.
(B) odd number of protons and odd number of neutrons.
(C) odd number of protons and even number of neutrons.
(D) equal numbers of protons and neutrons.

16. $^{232}_{90}$Th decays to $^{208}_{82}$Pb through a number of α and β emissions. Which of the following is true?

(A) Number of α-particles emitted is 8.
(B) Number of β-particles emitted is 6.
(C) Number of β-particles emitted is 8.
(D) Number of α-particles emitted is 6.

17. Which of the following nuclides is/are likely to be stable?

(A) $^{30}_{15}\text{P}$ (B) $^{24}_{12}\text{Mg}$

(C) $^{114}_{49}\text{In}$ (D) $^{114}_{48}\text{Cd}$

18. In a nuclear reactor heavy water is used to

(A) transfer the heat from the reactor.
(B) provide high speed neutrons for the fission reaction.
(C) reduce the speed of fast moving electrons.
(D) increase the speed of neutrons.

Assertion-Reasoning Type

Choose the correct option from the following:

(A) Statement 1 and Statement 2 are True, Statement 2 is the correct explanation of the Statement 1.
(B) Statement 1 and Statement 2 are True, Statement 2 is NOT a correct explanation of the Statement 1.
(C) Statement 1 is True, Statement 2 is False.
(D) Statement 1 is False, Statement 2 is True.

19. **Statement 1:** α rays can be stopped by air easily.
Statement 2: α rays are made of helium nuclei.

20. **Statement 1:** The reaction $^{8}_{5}\text{B} \rightarrow {}^{8}_{4}\text{Be}$ takes place due to positron decay.
Statement 2: n/p ratio increases in the above change.

Comprehension Type

Paragraph I

Radioactivity was discovered by Henri Becquerel in 1896, while investigating any possible relation between fluorescence and X-rays. A crystal of potassium uranyl sulphate was used as a source of fluorescence material. On exposure to sunlight, it emitted radiations which could penetrate paper, glass and aluminium sheets and ionize gases. These types of radiations were also observed in darkness. Nature and origin of these radiations were investigated by Becquerel, Rutherford, Pierre Curie and Marie Curie. Uranium changed to thorium during the emission of these radiations.

21. Consider following radioactive transformation:

A: $^{238}_{92}\text{U} \longrightarrow {}^{234}_{90}\text{Th}$

B: $^{234}_{90}\text{Th} \longrightarrow {}^{234}_{91}\text{Pa}$

C: $^{230}_{90}\text{Th} \longrightarrow {}^{230}_{90}\text{Th}$

Types of particles emitted are

(A) α, α, β (B) α, β, β
(C) α, β, γ (D) α, α, γ

22. How many α-and β-particles are emitted during following disintegration?

$$^{124}_{90}\text{Th} \longrightarrow {}^{206}_{82}\text{Pb}$$

(A) $7\alpha, 6\beta$ (B) $6\alpha, 6\beta$
(C) $6\alpha, 7\beta$ (D) $4\alpha, 4\beta$

23. Which is not the radioactive change in the following?

(A) $^{14}_{6}\text{C} \longrightarrow {}^{14}_{7}\text{N} + {}^{0}_{-1}e$

(B) $^{27}_{13}\text{Al} + {}^{4}_{2}\text{He} \longrightarrow {}^{30}_{15}\text{P} + {}^{1}_{0}n$

(C) $^{27}_{13}\text{Al} + 3\,{}^{1}_{1}\text{H} \longrightarrow \text{AlH}_3$

(D) $^{23}_{11}\text{Na} + {}^{2}_{1}\text{H} \longrightarrow {}^{24}_{11}\text{Na} + {}^{1}_{1}\text{H}$

Paragraph II

Earth's atmosphere is constantly being bombarded by cosmic rays of extremely high penetrating power. These rays, which originate in outer space, consist of electrons, neutrons, and atomic nuclei. One of the important reactions between the atmosphere and cosmic rays is the capture of neutrons by atmospheric nitrogen (nitrogen-14 isotope) to produce the radioactive carbon-14 isotope and hydrogen. The unstable carbon atoms eventually form $^{14}\text{CO}_2$, which mixes with the ordinary carbon dioxide ($^{12}\text{CO}_2$) in the air. As carbon-14 isotope decays, it emits β particles (electrons). The rate of decay (as measured by the number of electrons emitted per second) obeys first-order kinetics. It is customary in the study of radioactive decay to write the rate law as:

$$\text{Rate} = kN$$

where k is the first-order rate constant and N the number of ^{14}C nuclei present.

The carbon-14 isotopes enter the biosphere when carbon dioxide is taken up in plant photosynthesis. Plants are eaten by animals, which exhale carbon-14 in CO_2. Eventually, carbon-14 participates in many aspects of the carbon cycle. The ^{14}C lost by radioactive decay is constantly replenished by the production of new isotopes in the atmosphere. In this decay-replenishment process, a dynamic equilibrium is established whereby the ratio of ^{14}C to ^{12}C remains constant in living mater. But when an individual plant or an animal dies, the carbon-14 isotope in it is no longer replenished, so the ratio decreases as ^{14}C decays. This same change occurs when carbon atoms are trapped in coal, petroleum, or wood preserved underground and of course, in Egyptian mummies. After a number of years, there are proportionately fewer ^{14}C nuclei in, say, a mummy than in a living person.

24. Rock (geological dating) is based on the

(A) measurement of $^{238}U/^{206}Pb$ ratio.
(B) measurement of amount of ^{40}Ar gas that escapes, and comparing the amount of argon-40 with the amount of ^{40}K remaining in the sample.
(C) both of the above.
(D) none of the above.

25. The half-life of ^{40}K is 1.26×10^9 years and ratio of $^{40}Ar/^{40}K$ is 1.15 in the rock under study. Age of the rock is

(A) 1.39×10^9 years. (B) 2.54×10^8 years.
(C) 1.13×10^9 years. (D) 1.25×10^8 years.

26. Ra-226 decays with a half-life of 1.6×10^3 years. By using definition of curie, Avogadro's number is

(A) 6.1×10^{23} (B) 6.0×10^{23}
(C) 6.5×10^{23} (D) 5.9×10^{23}

Matrix-Match Type

27. Match the parameters with their values.

Column I	Column II
(A) Disintegration constant	(p) $1.44\ t_{1/2}$
(B) Average life	(q) 1 dps
(C) One curie	(r) $\dfrac{0.693}{t_{1/2}}$
(D) One Becquerel	(s) 3.7×10^{10} dps

28.

Column I	Column II
(A) Nuclear fusion	(p) $4n$ series
(B) Carbon dating	(q) $(4n + 3)$ series
(C) Thorium series	(r) Age of dead
(D) Actinium series	(s) Hydrogen bomb

ANSWER KEY

Mole Concept–I

1. (C) **2.** (D) **3.** (C) **4.** (B)
5. (A) **6.** (A) **7.** (A) **8.** (B)
9. (D) **10.** (B) **11.** (C) **12.** (A, B)
13. (A, B, D) **14.** (B, C) **15.** (A, B)
16. (A, D) **17.** (C) **18.** (D) **19.** (D)
20. (B) **21.** (C) **22.** (D) **23.** (C)
24. (C) **25.** (D) **26.** (C)
27. A → (p, r, s); B → (q); C → (r); D → (p)
28. A → (r); B → (p); C → (q, s); D → (p, q, s)

Mole Concept–II

1. (A) **2.** (C) **3.** (A) **4.** (A)
5. (C) **6.** (A) **7.** (B) **8.** (B)
9. (A) **10.** (A) **11.** (D) **12.** (A)
13. (B) **14.** (A) **15.** (A) **16.** (B, C)
17. (A, C) **18.** (A, C) **19.** (B, D) **20.** (B, D)
21. (B) **22.** (A) **23.** (A) **24.** (C)
25. (B) **26.** (A) **27.** (D) **28.** (C)
29. (D) **30.** (B) **31.** (B) **32.** (C)
33. (B) **34.** (A) **35.** (C)
36. A → (r); B → (s); C → (p); D → (t); E → (q)
37. A → (s); B → (q); C → (r); D → (p); E → (t)

Gaseous and Liquid State

1. (C) **2.** (B) **3.** (B) **4.** (C)
5. (D) **6.** (D) **7.** (A) **8.** (C)
9. (A) **10.** (A) **11.** (A) **12.** (B)
13. (B) **14.** (C) **15.** (C) **16.** (A, C)
17. (A, B) **18.** (A, C) **19.** (C) **20.** (A)
21. (C) **22.** (A)
23. A → (r); B → (s); C → (p); D → (q)
24. A → (q); B → (r); C → (s); D → (t); E → (p)

Solid State

1. (D) **2.** (A) **3.** (C) **4.** (C)
5. (D) **6.** (C) **7.** (B) **8.** (A)
9. (D) **10.** (C) **11.** (B) **12.** (A, C)
13. (B, C) **14.** (A, C, D) **15.** (A, C)
16. (B, C) **17.** (C) **18.** (C) **19.** (A)

20. (C) **21.** (B) **22.** (A) **23.** (C)
24. (B) **25.** (D) **26.** (A)
27. A → (r, s); B → (r, s); C → (p); D → (q)
28. A → (p); B → (q, s); C → (r)
29. A → (p); B → (q, s); C → (r); D → (q, s)

Atomic Structure

1. (B) **2.** (D) **3.** (C) **4.** (C)
5. (A) **6.** (D) **7.** (A) **8.** (A)
9. (A) **10.** (A) **11.** (B) **12.** (C)
13. (C) **14.** (A) **15.** (D)
16. (A, B, D) **17.** (A, B)
18. (B, C, D) **19.** (A, B)
20. (A, C, D) **21.** (B)
22. (B) **23.** (D)
24. (A) **25.** (A)
26. (B) **27.** (D)
28. (A) **29.** (C)
30. (B) **31.** (D)
32. A → (r); B → (q); C → (s); D → (p)
33. A → (r); B → (q, r); C → (q, s); D → (p, q, s)

Chemical Bonding

1. (D) **2.** (D) **3.** (C) **4.** (C)
5. (C) **6.** (A) **7.** (C) **8.** (A)
9. (A) **10.** (D) **11.** (C) **12.** (B)
13. (D) **14.** (D) **15.** (B) **16.** (A)
17. (B) **18.** (D) **19.** (B) **20.** (B)
21. (B, C, D) **22.** (A, B, C)
23. (B, D) **24.** (C, D)
25. (A, C, D) **26.** (C)
27. (B) **28.** (A)
29. (A) **30.** (A) **31.** (A) **32.** (A)
33. (B) **34.** (D) **35.** (C) **36.** (C)
37. A → (q, r, s); B → (p, q, r, s); (C) → (q, s); (D) → (p, s)
38. A → (p, q); (B) → (p, q, r); (C) → (p, q, r, s); (D) → (p, q, r, s)

Chemical Energetics

1. (C) **2.** (A) **3.** (A) **4.** (A)
5. (C) **6.** (A) **7.** (A) **8.** (D)
9. (B) **10.** (B) **11.** (A) **12.** (B)
13. (A) **14.** (A) **15.** (B) **16.** (D)
17. (B, D) **18.** (A, C, D)
19. (A, B, C) **20.** (A, C)
21. (A, B) **22.** (A, B, C, D) **23.** (A, B)
24. (D) **25.** (E) **26.** (A) **27.** (E)
28. (A) **29.** (A) **30.** (B) **31.** (B)
32. (B) **33.** (D)

34. A → (p, q, r, s); B → (r, q); C → (p, q); D → (r, s)
35. A → (s); B → (r); C → (p); D → (q)

Solutions

1. (C) **2.** (B) **3.** (B) **4.** (C)
5. (D) **6.** (B) **7.** (C) **8.** (A)
9. (A) **10.** (D) **11.** (C) **12.** (B)
13. (B) **14.** (A) **15.** (C) **16.** (D)
17. (C) **18.** (B) **19.** (B, C) **20.** (A, C)
21. (A, C, D) **22.** (A, B, C, D)
23. (A) **24.** (A) **25.** (B) **26.** (A)
27. (B) **28.** (A) **29.** (B) **30.** (B)
31. (B) **32.** (A)
33. (A) → (q); (B) → (p); (C) → (r, s); (d) → (p)

Chemical Equilibrium

1. (B) **2.** (B) **3.** (B) **4.** (A)
5. (B) **6.** (A) **7.** (C) **8.** (B)
9. (C) **10.** (A) **11.** (D) **12.** (D)
13. (A) **14.** (D) **15.** (C) **16.** (A, C)
17. (A, C, D) **18.** (C, D) **19.** (C)
20. (D) **21.** (C) **22.** (C) **23.** (A)
24. (B) **25.** (A) **26.** (B) **27.** (C)
28. A → (p, q, r, s); B → (q); C → (p, q, r, s); D → (p, q, r)
29. A → (r); B → (p, q); C → (q, s); D → (p, r)

Ionic Equilibrium

1. (C) **2.** (A) **3.** (B) **4.** (A)
5. (A) **6.** (A) **7.** (A) **8.** (A)
9. (A) **10.** (C) **11.** (A) **12.** (A)
13. (A) **14.** (B) **15.** (A) **16.** (B)
17. (B) **18.** (A) **19.** (B) **20.** (A)
21. (B) **22.** (C) **23.** (B) **24.** (D)
25. (A, B) **26.** (A, D) **27.** (A, D) **28.** (A, B, C)
29. (C, D) **30.** (A, C, D) **31.** (C, D) **32.** (A, C)
33. (B) **34.** (A) **35.** (D) **36.** (A)
37. (D) **38.** (C) **39.** (A) **40.** (A)
41. (A) **42.** (A) **43.** (D) **44.** (A)
45. A → (q); B → (s); (C) → (p, q, r); D → (p)
46. A → (q); B → (r); (C) → (s); (D) → (p)
47. A → (r); B → (s); (C) → (p); (D) → (q)

Electrochemistry

1. (A) **2.** (A) **3.** (C) **4.** (A)
5. (C) **6.** (B) **7.** (D) **8.** (D)
9. (C) **10.** (B) **11.** (B) **12.** (A)

13. (A) **14.** (C) **15.** (C) **16.** (B)
17. (A) **18.** (A) **19.** (A, D) **20.** (A, C)
21. (A, B, D) **22.** (B, C, D) **23.** (A, C)
24. (A, B, C, D) **25.** (D) **26.** (B)
27. (B) **28.** (D) **29.** (D) **30.** (C)
31. (B) **32.** (D) **33.** (A) **34.** (C)
35. (B)
36. A → (p, q, r); B → (p, q, r); C → (p, r); D → (p, q, r)
37. A → (p, q, r, s); B → (p, q); C → (p, q, r, s); D → (p, q, r, s)
38. A → (p, s); B → (q, r); C → (p, s); D → (q, s)

Chemical Kinetics

1. (B) **2.** (B) **3.** (B) **4.** (A)
5. (C) **6.** (A) **7.** (B) **8.** (B)
9. (C) **10.** (B) **11.** (D) **12.** (B)
13. (D) **14.** (C) **15.** (A) **16.** (A)
17. (B) **18.** (A, D) **19.** (B, C) **20.** (A, C)
21. (A, B, D) **22.** (C) **23.** (B)
24. (C) **25.** (A) **26.** (A) **27.** (B)
28. (D) **29.** (B) **30.** (A)
31. A → (p, q, r, s); B → (q, r, s); C → (p, q, r, s); D → (r, s)
32. A → (s); B → (r); C → (p); D → (q)
33. A → (p, q); B → (r, p); C → (s)

Surface Chemistry

1. (C) **2.** (A) **3.** (B) **4.** (A)
5. (C) **6.** (C) **7.** (A) **8.** (B)
9. (C) **10.** (C) **11.** (C) **12.** (B, C, D)
13. (A, B, C) **14.** (B, C, D) **15.** (A, B)
16. (A, B, C) **17.** (A, C) **18.** (C, D)
19. (A) **20.** (A) **21.** (A) **22.** (A)
23. (A) **24.** (B) **25.** (A) **26.** (C)
27. (A)
28. A → (p, q); B → (r); C → (q, t); D → (s); E → (u)
29. A → (q); B → (q); C → (s); D → (r); E → (t)

Nuclear Chemistry

1. (D) **2.** (C) **3.** (B) **4.** (A)
5. (B) **6.** (A) **7.** (B) **8.** (A)
9. (D) **10.** (A) **11.** (D) **12.** (C)
13. (C) **14.** (D) **15.** (A, D) **16.** (B, D)
17. (B, D) **18.** (A, C) **19.** (B) **20.** (B)
21. (C) **22.** (A) **23.** (C) **24.** (C)
25. (B) **26.** (A)
27. A → (r); B → (p); C → (s); D → (q)
28. A → (s); B → (r); C → (p); D → (q)

APPENDIX

B

Additional Practice Problems

MOLE CONCEPT–I

1. In a certain region of space there are only 5 molecules per cm^3 on an average. The temperature is 3 K. What is the average pressure of this very dilute gas?

2. A sample of clay was partially dried and then contained 50% silica and 7% water. The original clay contained 12% water. Find the percentage of silica in the original sample.

3. Zinc metal reacts with hydrochloric acid by the following reaction:

$$Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$$

If 0.30 mol Zn is added to hydrochloric acid containing 0.52 mol HCl. How many moles of H_2 are produced?

4. 10 mL of a mixture of CH_4, C_2H_4 and CO_2 were exploded with excess of air. After explosion, there was contraction of 17 mL on cooling and after treatment with KOH, there was further reduction of 14 mL. What is the composition of the mixture?

5. A mixture of FeO and Fe_3O_4 when heated in air to a constant weight, gains 5% in its weight. Find the composition of the initial mixture. (Fe = 56, O = 16)

6. Reaction of 1 g of a sample containing, NaCl, NaBr and inert material, with excess of $AgNO_3$, produces 0.526 g of precipitate of AgCl and AgBr. By heating this precipitate, in a current of chlorine, AgBr converted to AgCl and the precipitate then weighted 0.426 g. Find the percentage of NaCl and NaBr in the sample.

7. One liter of milk weighs 1.035 kg. The butter fat is 4% in volume of milk and has density of 875 kg m^{-3}. Find the density of fat free skimmed milk.

8. Polyethylene can be produced from CaC_2 according to the following sequence of reactions.

$$CaC_2 + H_2O \rightarrow CaO + C_2H_2$$

$$C_2H_2 + H_2 \rightarrow C_2H_4$$

$$nC_2H_4 \rightarrow (CH_2CH_2)_n$$

Calculate the mass of polyethylene which can be produced from 20 kg of CaC_2. Assume that the % yield of each step is 50%.

MOLE CONCEPT–II

9. A 0.5 g sample of an iron-containing mineral mainly in the form of $CuFeS_2$ was reduced suitably to convert all the ferric iron into ferrous form and was obtained as a solution. In the absence of any interfering matter, the solution required 42 mL of 0.01 M $K_2Cr_2O_7$ solution for titration. Calculate the percentage of $CuFeS_2$ in the mineral. (At. wt. of Cu = 63.5, Fe = 55.8, S = 32, O = 16)

10. One liter of O_2 at STP was passed through an ozonizer when the resulting volume was 888 mL at STP. This quantity of ozonized oxygen was passed through excess of KI solution. Calculate the weight of I_2 liberated. Given the reaction:

$$O_3 + 2KI + H_2O \rightarrow 2KOH + I_2 + O_2$$

11. A 0.5 g sample containing MnO_2 is treated with HCl, liberating Cl_2. The Cl_2 is passed into a solution of KI and 30.0 cm^3 of 0.1 M $Na_2S_2O_3$ are required to titrate the liberated iodine. Calculate the percentage of MnO_2 in the sample. (At. wt. of Mn = 55)

12. 0.5 g mixture of $K_2Cr_2O_7$ and $KMnO_4$ was treated with excess of KI in acidic medium. Iodine liberated required 100 cm^3 of 0.15 M sodium thiosulphate solution for titration. Find the percent amount of each in the mixture. (At. wt. of K = 39, Cr = 52, Mn = 55, Na = 23, S = 32)

13. H_2O_2 is reduced rapidly by Sn^{2+}, the products being Sn^{4+} and water. H_2O_2 decomposes slowly at room temperature to yield O_2 and water. Calculate the volume of O_2 produced at 20ºC and 1 atm when 200 g of 10% by mass H_2O_2 in water is treated with 100 mL of 2M Sn^{2+} and then the mixture is allowed to stand until no further reaction occurs.

14. A substance of crude copper is boiled in H_2SO_4 till all the copper has reacted. The impurities are inert to the acid. The SO_2 liberated in the reaction is passed into 100 mL of 0.4 M acidified $KMnO_4$ ($SO_2 \rightarrow SO_4^{2-}$). The solution of $KMnO_4$ after passage of SO_2 is allowed to react with oxalic acid and requires 25 mL of 1 M oxalic acid. If the purity of copper is 95.25%, what was the weight of the sample?

15. A mixture containing equal moles of CuS and Cu_2S was treated with 100 mL of 1.5 M $K_2Cr_2O_7$. The products obtained were Cr^{3+}, Cu^{2+} and SO_2. The excess oxidant was reacted with 50 mL of Fe^{2+} solution of 25 mL of the same Fe^{2+} solution required 0.3 M acidic $KMnO_4$, the volume of which used was 20 mL. Calculate moles of each substance in original mixture.

16. A 458 g sample containing Mn_3O_4 was dissolved and all manganese was converted to Mn^{2+}. In the presence of fluoride ion, Mn^{2+} is titrated with 3 L of $KMnO_4$ solution (which was 1.25 N against oxalate in acidic medium), both reactants being converted to a complex of Mn (III). What was the percentage of Mn_3O_4 in the sample?

17. 0.5 g of fuming H_2SO_4 (oleum) is diluted with water. The solution requires 30 mL of 0.4 N NaOH for complete neutralization. Find the percentage of free SO_3 in the sample of oleum.

18. A 2.024 g sample containing $Ba(SCN)_2$ was dissolved in a bicarbonate solution. 50 mL of 1 N iodine solution was added, and the mixture was allowed to stand for 5 min. The solution was then acidified, and the excess I_2 was titrated with 26 mL of 1 M sodium thiosulphate. Write a balanced equation for the oxidation of SCN^-, SO_4^{2-} and HCN. Calculate the percentage of $Ba(SCN)_2$ in the sample.

LIQUID AND GASEOUS STATE

19. 2 mol of Ne gas and 5 mol of He gas, both samples having average velocity 7×10^2 ms^{-1}, are mixed. Find the average translational kinetic energy per mol of the given gas mixture (in joules). Report your answer as x where x = (average translational KE in joules) × 0.002. The reported answer should be up to the nearest integer.

20. A 1 L gas mixture of CO, CO_2 and N_2 was mixed with 1 L O_2 and allowed to burn completely. The product gas mixture, when passed subsequently through KOH solution and alkaline pyragallol solution, suffered a total contraction of 1.6 L. On the other hand, if the product gas mixture was mixed with excess of CO gas and again allowed to burn, the new product mixture suffered a contraction of 2.3 L on passing through KOH solution. Find the volume percentage of CO in the initial mixture. Report your answer as y where y = (Volume % of CO)/10.

21. A flask of 8.96 L capacity contains a mixture of N_2 and H_2 at 273 K and 1 atm pressure. If the mixture is made to react to form NH_3 gas at the same temperature, the pressure in the flask reduces to 0.85 atm. Find the partial pressure of NH_3 gas in the final mixture in atm. Report your answer as y where y = (Partial pressure of NH_3) × 20.

22. Find the number of diffusion steps required to separate the isotopic mixture initially containing some amount of H_2 gas and 1 mol of D_2 gas in a container of 3 L capacity maintained at 24.6 atm and 27ºC to the final mass ratio $\left(\frac{w_{D_2}}{w_{H_2}}\right)$ equal to $\frac{1}{4}$.

23. What is the ratio of the number of molecules having speeds in the range of $2u_{mp}$ and $2u_{mp} + du$ to the number of molecules having speeds in the range of u_{mp} and $u_{mp} + du$?

24. One mol of an ideal gas is subjected to a process in which $p = \frac{1}{8.21}V$, where p is in atm and V in L. If the process is operating from 1 atm to finally 10 atm (no higher pressure achieved during the process) then what would be the maximum temperature obtained and at what instant will it occur in the process?

25. A mixture of H_2O(vap), CO_2 and N_2 was trapped in a glass apparatus with a volume of 0.731 mL. The pressure of total mixture was 1.74 mm Hg at 23°C. The sample was transferred to a bulb in contact with dry ice (–75°C) so that H_2O(vap) are frozen out. When the sample returned to normal value of temperature, pressure was 1.32 mm Hg. The sample was then transferred to a bulb in contact with liquid N_2 (–95°C) to freeze out CO_2. In the measured volume, pressure was 0.53 mm Hg at original temperature. How many moles of each constituent are present in the mixture?

26. Radius of a spherical molecule of a gas is 2×10^{-8} cm. Calculate:

(a) co-volume per molecule.

(b) co-volume per mole.

(c) critical volume.

27. A gas is present in a container connected to frictionless, weightless piston operating always at one atmosphere pressure such that it permits flow of gas outside (with no adding of gas). The graph of n vs. T (Kelvin) was plotted and was found to be a straight line with coordinates of extreme points as (300, 2) and (200, 3). Calculate:

(a) relationship between n and T.

(b) relationship between V and T.

(c) maxima or minima value of V.

SOLID STATE

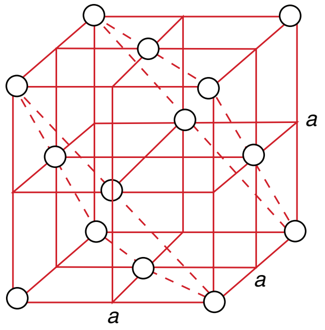
28. Metallic gold crystallizes in the face-centered cubic lattice. The length of the cubic unit cell $a = 4.070$ Å.

(a) What is the closest distance between gold atoms?

(b) How many nearest neighbors does each gold atom have at the distance calculated in (a)?

(c) What is the density of gold?

(d) Prove that the packing fraction for gold, the fraction of the total volume occupied by the atom themselves, is 0.74.



29. Find the size of largest sphere that will fit in the octahedral void in an ideal fcc crystal as a function of atomic radius r. The insertion of this sphere into void does not distort the fcc lattice. Calculate the packing fraction of fcc lattice when all the octahedral voids are filled by this sphere.

30. Potassium crystallizes in a body-centered cubic lattice with edge length, $a = 5.2$ Å.

(a) What is the distance between nearest neighbors?

(b) What is the distance between next nearest neighbors?

(c) How many nearest neighbors does each K atom have?

(d) How many next nearest neighbors does each K atom have?

(e) What is the calculated density of crystalline potassium?

31. If NaCl is dopped with 10^{-3} mol % $SrCl_2$, what is the numbers of cation vacancies per mole of NaCl?

32. The mineral hawleyite, one form of CdS, crystallizes in one of the cubic lattices, with edge length 5.87 Å. The density of hawleyite is 4.63 g cm^{-3}.

(a) In which cubic lattice does hawleyite crystallize?

(b) Find the Schottky defect in g cm^{-3}.

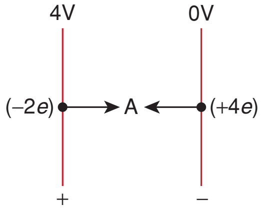
33. A strong current of trivalent gaseous boron passed through a germanium crystal, decreases the density of the crystal due to partial replacement of germanium by boron and due to interstitial vacancies created by missing Ge atoms. In one such experiment, one gram of germanium is taken and the boron atoms are found to be 150 ppm by weight, when the density of the Ge crystal decreases by 4%. Calculate the percentage of missing vacancies due to germanium, which are filled up by boron atoms.

(At. wt. of Ge = 72.6, B = 11)

ATOMIC STRUCTURE

34. Find out the number of waves made by a Bohr electron in one complete revolution in its third orbit.

35. In the assembly as shown in the figure below, the potential difference across the plates is 4 V. A positive particle of charge $+4e$ is projected from the negative plate with an initial kinetic energy of 4 eV and the negative particle of charge $(-2e)$ is projected from the positive plate. Both the particles reach point A with zero kinetic energy. Find the initial kinetic energy of the negative particle in eV.



36. Electrons in a sample of H atoms make transitions from state $n = x$ to some lower excited state. The emission spectrum from the sample is found to contain only the lines belonging to a particular series. If one of the photons had energy of 0.6375 eV, then, find the value of x.

$$\left[\text{Take } 0.6375\,\text{eV} = \frac{3}{4} \times 0.85\text{ eV}\right]$$

37. A hydrogen like atom (atomic number Z) is in a higher excited state of quantum number n. This excited atom can make a transition to the first excited state by successively emitting two photons of energies 10.20 eV and 17.00 eV respectively. Alternatively, the atom from the same excited state can make a transition to the second excited state by successively emitting two photons of energy 4.25 eV and 5.95 eV respectively. Determine the values of n and Z (ionization energy of hydrogen atom = 13.6 eV).

38. In a sample of hydrogen atom in ground state, electrons make transition from ground state to a particular excited state where path length is five times de-Broglie wavelength, electrons make back transition to the ground state producing all possible photons. If photon having second highest energy of this sample can be used to excite the electron in a particular excited state of Li^{2+} atom then find the final excited state of Li^{2+} atom.

39. A chemist has one mole of H-atoms. He finds that on absorption of 410 kJ, half of X-atoms transfer one electron to the other half. If all the resulting X^- ions are subsequently converted to X^+ ions, an addition of 735 kJ is required. Find the electron affinity of X.

40. **(a)** The wave function of 2s electron is given by

$$\psi_{2s} = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{\frac{3}{2}}\left(2 - \frac{r}{a_0}\right)e^{-\frac{r}{a_0}}$$

It has a node at $r = r_0$. Find relation between r_0 and a_0.

(b) Find wavelength for 100 g particle moving with velocity 100 ms^{-1}.

41. The radial wave function for 1s orbit for a single electron species is given by $\psi_r = ke^{\frac{-\sigma}{2}}$, where $\sigma = \dfrac{2Zr}{na_0}$ and k is a constant (a_0 = radius of first Bohr's orbital in H-atom = 52.9 pm, n = principal quantum number). Calculate the most probable distance of 1s electron in Be^{3+} ion. Give your answer in the form of most probable distance in pm × 1000.

42. Consider a sample containing 100 identical H-like atoms (hypothetical atoms, Z can be fractional) such that:

(i) Out of the given atoms, some are in ground state and some others are in a higher energy level ($n = x$) and the potential energy of electron in the ground state of given atom is –192 eV.

(ii) When the sample is exposed to radiations of wavelength 155 nm, the electrons jump to another higher energy level ($n = x + 3$). Upon back transition upto ground state, a total of 10 different spectral lines are produced.

Answer the following two questions:

(a) What is the final state in which the electrons move after absorbing photons of wavelength 155 nm?

(b) What is the maximum number of atoms which had their electron in ground state initially?

Take $hc = 12400$ eV/Å.

43. Magnetic moment of X^{3+} ion of $3d$ series is $\sqrt{35}$ B.M. What is atomic number of X^{3+}?

44. Two hydrogen atoms collide head on and end up with zero kinetic energy. Each then emits a photon with a wavelength 121.6 nm. Which transition leads to this wavelength? How fast were the hydrogen atoms travelling before the collision? (Given: $R_H = 1.097 \times 10^{27}$ m^{-1} and $m_H = 1.67 \times 10^{-27}$ kg.)

45. 1.53 g of hydrogen is excited by irradiation. At a certain instant, 10% of the atoms are at the excited level of energy –328 kJ mol^{-1} and 2% of the atoms are at the excited level of energy –146 kJ mol^{-1}. The remaining atoms are in the ground state. Calculate how much energy will be evolved when all the excited atoms return to the ground state.

46. The photochemical dissociation of oxygen results in the production of two oxygen atoms, one in the ground state and one in the excited state $O_2 \xrightarrow{h\nu} O + O^*$. The maximum wavelength λ, needed for this is 174 nm and the excitation energy of $O \rightarrow O^{\bullet}$ is 3.15×10^{-19} J. How much energy in kJ mol^{-1} is needed for the dissociation of one of oxygen into normal (i.e., ground state) atoms?

47. Electrons of energy 12.1 eV are fired at the hydrogen atom in a gas discharge tube. Determine the wavelength of the lines that can be emitted by hydrogen.

48. A single electron atom has nuclear charge $+Ze$ where Z is atomic number and e is electronic charge. It requires 47.2 eV to excite the electron from the second Bohr orbit to third Bohr orbit. Find:

(a) The atomic number of element.

(b) The energy required for transition of electron from third to fourth orbit.

(c) The wavelength required to remove electron from first Bohr orbit to infinity.

(d) The kinetic energy of electron in first Bohr orbit.

49. The de Broglie wavelength of electron of He^+ ion is 3.329 Å. If the photon emitted upon de-excitation of this He^+ ion is made to hit H-atom in its ground state so as to liberate electron from it, what will be the de-Broglie's wavelength of photoelectron?

50. The subshell that arises after f is called g subshell.

(a) How many g orbitals are present in the g subshell?

(b) In what principal electronic shell, would the g subshell first occur and what is the total number of orbitals in this principal shell?

51. Quantum efficiency, ϕ is defined as

$$\phi = \frac{\text{No. of molecules reacted}}{\text{No. of photons absorbed}}$$

A glass vessel containing large quantities of H_2(g) and Cl_2(g) is irradiated with a wavelength of 500 nm with a quantum efficiency equal to 10^4. The entire vessel absorbed 10 J of energy. After the irradiation the gas mixture remaining in the vessel is washed with 100 L of water thoroughly. What will be the pH of the wash water in nearest possible integer?
(Given: $N_A = 6 \times 10^{23}$; $c = 3 \times 10^8$ m s^{-1};
$h = 6.625 \times 10^{-34}$ J s)

CHEMICAL BONDING

52. Give explanation for the following.

(a) $BeCl_2$ shows a high degree of covalence in its reactions, whereas $BaCl_2$ is predominantly ionic.

(b) The H—P—H angle in PH_3 is smaller than that H—N—H angle in NH_3.

(c) The bond angle in H_2S is smaller than that in H_2O.

(d) The hydrogen bonding in HF is stronger than in H_2O but the boiling point of water is 100ºC, while that of HF is only 19.5ºC.

(e) The boiling points of water (100ºC) and HF (19.5º) are quite high as compared to NH_3 which is only –33.4ºC.

(f) Carbon-oxygen bond lengths in formic acid are 1.23 Å and 1.36 Å and both oxygen bonds in sodium formate have the same value, that is, 1.27 Å.

(g) Valency of oxygen is generally two whereas sulphur shows valency of two, four and six.

(h) Three carbon oxygen bonds are having equal length in carbonate ion.

(i) Although Cl has the same electronegativity as nitrogen but it does not form effective H-bonding.

(j) Bond order in N_2 is 3 whereas it is 2.5 in NO.

(k) The super oxides KO_2, RbO_2, and CsO_2 are paramagnetic.

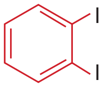
(l) Sigma bond is stronger than π-bond.

(m) NF_3 is weaker base than NH_3, NCl_3, NBr_3, and NI_3.

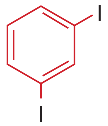
(n) NO molecule is paramagnetic.

53. Assuming the additivity of covalent radii in the C—I bond, what would be the iodine-iodine distance in each of the following di-iodobenzenes? Assume that the ring is regular hexagon and that each C—I bond lies on a line through the center of the hexagon. (Take C—C bond-length = 1.40 Å, radius atom = 1.33 Å, radius of carbon atom = 0.77 Å.)

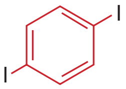
(a)



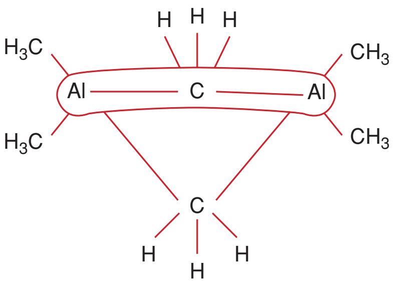
(b)



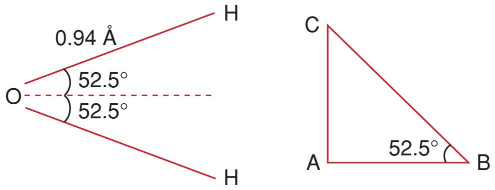
(c)



54. Carbon has maximum covalency of four. Explain the covalency of carbon in the given compound.



55. Dipole moment of H_2O is 1.85 D. If bond angle is 105° and O—H bond length is 0.94 Å, determine the magnitude of the charge on the oxygen atom in the water molecule.

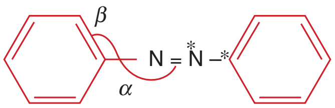


56. Dipole moment of HX is 2.59×10^{-30} C m. Bond length of HX is 1.39 Å. Calculate percentage ionic character of molecule.

57. Azobenzene, $(C_6H_5)_2N_2$, is an important starting material in the production of dyes.

(a) Describe the hybridization scheme for the atoms marked with (*).

(b) Indicate the value of the bond angles labeled α and β.



58. Describe and compare the geometries of the molecules and the hybridization of the carbon and boron atoms in $F_2C{=}C{=}CF_2$ and $F_2B{-}C{\equiv}C{-}F_2B$. Compare the relative orientation of the sets of fluorine atoms in the two cases. In which case is it impossible for all four fluorine atoms to lie in the same plane?

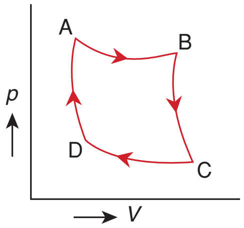
59. A diatomic molecule has a dipole moment of 1.2 D. If the bond distance is 1.0 Å, what fraction of an electronic charge, *e*, exists on each atom?

60. The HF_2^- ion exists in the solid state and also in liquid HF solution, but not in dilute aqueous solution. Explain.

CHEMICAL ENERGETICS

61. 3.5 g of a fuel (with molecular weight 28), was burnt in a calorimeter and raised the temperature of 1 g water from 25°C to 67.3°C. If all the heat generated was used in heating water, calculate heat of combustion of fuel.

62. An ideal monoatomic gas is working substance in a Carnot cycle shown below.



Gas absorbed 160 J heat during isothermal reversible process from A to B. Volume of gas is 2 L at B and it changes to 16 L during adiabatic expansion from B to C. Some heat is lost by gas during isothermal compression from C to D and then gas reaches to state A from D through adiabatic compression. Amount of heat lost by working substance during compression C to D is given to another monoatomic ideal gas G undergoing an expansion from 2 L to 5 L in a process defined as $p = V^2$. Find change in temperature of gas G.

63. A certain amount of ideal gas, present in a uniform, piston-fitted cylinder is allowed to expand under reversible, isothermal condition, to a final state and deliver some work on the surroundings. The height of piston before and after expansion was 10 cm and 50 cm, respectively. By what distance, the piston will be required to move in upward direction so that half of the work of the previous process is delivered.

64. Consider an ideal gas contained in a cylinder and separated by a frictionless adiabatic piston into two sections, A and B. Section B is in contact with water bath that maintains it at constant temperature. Initially,

$T_A = T_B = 300$ K, $V_A = V_B = 2.00$ L and $n_A = n_B = 2.00$ mol

Heat is supplied in section A and the gas expands, moving the piston to the right, that is, compressing section B until the final volume in section B is 1.00 L. Using $C_{V,m} = 20$ J K^{-1} mol^{-1}. Calculate:

(a) the work done by the gas in section A.

(b) ΔU (change in internal energy) in section B.

(c) q for the gas in section B.

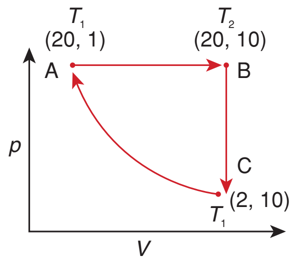
(d) ΔU for gas in section A and q for gas in A.

65. Calculate the resonance energy of N_2O from the following data:

$\Delta_f H^\circ(N_2O)$ = 82 kJ mol^{-1}; $\Delta_f H^\circ(N{\equiv}N)$ 946 kJ mol^{-1}; $\Delta_f H^\circ(N{=}N)$ 418 kJ mol^{-1}; $\Delta_f H^\circ(O{=}O)$ 498 kJ mol^{-1}; $\Delta_f H^\circ(N{=}O)$ 607 kJ mol^{-1}

66. Consider a class room that is roughly 5 m × 10 m × 3 m. Initially, $T = 20$ºC and $p = 1$ atm. There are 50 people in the class, each losing energy to the room at the average rate of 150 watt. Assume that the walls, ceiling, floor, and furniture are perfectly insulated and do not absorb any heat. How long will the physical chemistry examination last if the professor has foolishly agreed to dismiss the class when the air temperature in the room reaches body temperature, 37°C? For air, $C_p = \frac{7}{2}R$. Loss of air to the outside, as the temperature rises may be neglected.

67. One mole of a perfect monoatomic gas is put through a cycle consisting of the following three reversible steps:



(i) Isothermal compression from 2 atm and 10 L to 20 atm and 1 L.

(ii) Isobaric expansion to return the gas to the original volume of 10 L with T going from T_1 to T_2.

(iii) Cooling at constant volume to bring the gas to the original pressure and temperature.

The steps are shown schematically in the above figure.

(a) Calculate T_1 and T_2.

(b) Calculate ΔU, q and w in calories, for each step.

68. Find value of ΔG, for following transformation

$$\underset{\substack{T = 263.15\text{ K} \\ (1\text{ mol})}}{H_2O(l)} \rightarrow \underset{T = 263.15\text{ K}}{H_2O(s)}$$

Given: C_p of $H_2O(l)$ = 75.312 J K^{-1} mol^{-1}

C_p of $H_2O(s)$ = 36.401 J K^{-1} mol^{-1}

$\Delta_{\text{freez}} H = -6008.2$ J mol^{-1}; $\ln \dfrac{273.15}{263.15} = 0.0373$

69. 10 g of neon initially at a pressure of 506.625 kPa and temperature at 473 K expands adiabatically to a pressure at 202.65 kPa. Calculate the entropy change of the system and total entropy change for the following ways of carrying out this expansion.

(a) Expansion is carried out reversibly.

(b) Expansion occurs against a constant external pressure of 206.65 kPa

(c) Expansion is a free expansion.

70. Only N_2, CO and CO_2 gases remain after 0.72 g of carbon is treated with 1 L of air at 27°C and 4.92 atm pressure. Assume air composition O_2 = 0%, N_2 = 79% and CO_2 = 1% (by volume). The heat evolved (in kcal) under constant pressure is:

Given:

$$C + O_2 \longrightarrow CO_2, \quad \Delta H = -100 \text{ kcal mol}^{-1}$$
$$C + O_2 \longrightarrow CO, \quad \Delta H = -25 \text{ kcal mol}^{-1}$$

71. Heat supplied to the carnot engine is 37.3 kJ. How much useful work in kJ can be done by engine which works between 10°C and 100°C?

72. A liquid in container is compressed from (2 atm, 1 L) to (10 atm, 0.5 L) isothermally where it absorbs 200 J heat and work done on the system is 500 J. Calculate the enthalpy change of process in kJ. (1 atm × 1 L = 100 J).

73. Reaction of gaseous fluorine (F_2) with compound X yields a single product Y, whose mass precent composition is 61.7%F and 38.3% Cl. Calculate $\Delta_r H°$ (in kJ mol^{-1}) for the synthesis of Y using following information

$$2ClF_3(g) + O_2(g) \longrightarrow Cl_2O(g) + OF_2(g); \quad \Delta_f H° = 205.6 \text{ kJ}$$

$$2ClF_3(g) + 2O_2(g) \longrightarrow Cl_2O(g) + 3OF_2(g); \quad \Delta_f H° = 533 \text{ kJ}$$

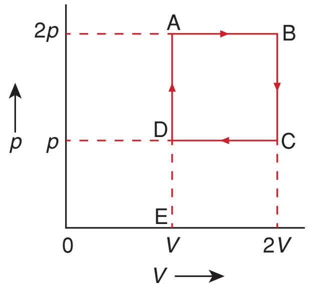
$$\Delta_f H°(OF_2, g) = 24.7 \text{ kJ mol}^{-1}$$

74. The heat of combustion of ethene gas is 330 kcal mol^{-1}. Calculate bond $>\mathrm{C}=\mathrm{C}<$ energy (in kcal mol^{-1}) of compound assuming that bond energy of C—H bond is 93.6 kcal mol^{-1}.

Given: $\Delta_f H°$ for CO_2 (g) and H_2O (l) are –94.2 and –61 kcal mol^{-1} respectively. Heat of atomization of carbon and hydrogen are 150 and 51.5 kcal mol^{-1} respectively.

75. 1 mol of a liquid of molar volume 100 mL is kept in an adiabatic container under a pressure of 1 bar. The pressure is steeply increased to 100 bar. Under this constant pressure of 100 bar, the volume of the liquid decreases by 1 mL. Calculate ΔU and ΔH of the process.

76. The state of a mole of an ideal gas changed from state A ($2p$, V) through four different processes and finally returns to initial state A reversibly as shown below.



Calculate the total work done by the system and heat absorbed by the system, in the cyclic process.

SOLUTIONS

77. A current of dry air is passed through a bulb containing 5 g of a solute in 100 g of water and then through water alone. The losses in weight of the solution and pure water were respectively 0.78 g and 0.02 g. Calculate (a) relative lowering of vapor pressure and (b) molecular weight of solute.

78. 1000 g of 1 molal sucrose solution in water is cooled to –3.534ºC. What weight of ice would be separated out at this temperature? K_f (H_2O) = 1.86 K kg mol^{-1}.

79. A 10% solution of cane sugar has undergone partial inversion according to the reaction:

$$\text{Sucrose} + \text{Water} \longrightarrow \text{Glucose} + \text{Fructose}$$

If the boiling point of solution is 100.27°C.

(a) What is the average mass of the dissolved materials?

(b) What fraction of the sugar has inverted? $K_b(H_2O)$ = 0.512 K mol^{-1} kg

80. A complex is represented as $CoCl_3{\cdot}xNH_3$. Its 0.1 molal solution in aqueous solution shows ΔT_f = 0.558°C. K_f for H_2O is 1.86 K mol^{-1} kg. Assuming 100% ionization of complex and coordination number of Co as six, calculate formula of the complex.

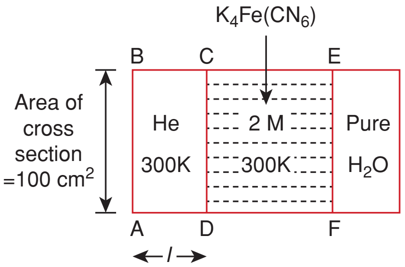
81. A mixture of two immiscible liquids (water and nitrobenzene) boils at 372 K and the vapor pressure at this temperature are 97.7 kPa (H_2O) and 3.6 kPa ($C_6H_5NO_2$). Calculate the weight % of nitrobenzene in the vapor.

82. The vapor pressure of a certain liquid is given by the equation:

$$\log_{10} p = 3.54595 - \frac{313.7}{T} + 1.40655 \log_{10} T$$

where p is the vapor pressure in mm of Hg and T is temperature in Kelvin. Determine the molar latent heat of vaporization as a function of temperature. Calculate its value at 80 K.

83.



CD : Fixed wall, EF : semipermeable membrane (SPM), fixed wall : allows the pressure transfer but no mass transfer. If 16 g of helium is present in ABCD chamber, calculate the length of this chamber in cm if no osmosis takes place through SPM EF. Assume 75% ionization of $K_4[Fe(CN)_6]$.

84. If osmotic pressure of 1 M aqueous solution of H_2SO_4 at 500 K is 90.2 atm. Calculate K_{a2} of H_2SO_4. Give your answer after multiplying 1000 with K_{a2}, assuming ideal solution. (Given: K_{a1} of H_2SO_4 is infinity, $R = 0.082$ L atm mol^{-1} K^{-1}.)

85. Assume liquefied petroleum gas (LPG) is a 50 – 50% mol mixture of *n*-pentane and *n*-butane. Calculate the calorific value (in kJ mol^{-1}) of gas available from a newly filled cylinder.

	n-butane, C_4H_{10}	*n*-pentane, C_5H_{12}
Vapor pressure	1800 torr	600 torr
Calorific value	2800 kJ mol^{-1}	3600 kJ mol^{-1}

CHEMICAL EQUILIBRIUM

86. When NO and NO_2 are mixed, the following equilibrium is obtained:

$$2NO_2 \rightleftharpoons N_2O_4;\ K_p = 6.8\ \text{atm}^{-1}$$

and $NO + NO_2 \rightleftharpoons N_2O_3$

In an experiment when NO and NO_2 are mixed in the ratio of 1 : 2 the final pressure was 5.05 atm and the partial pressure of N_2O_4 was 1.7 atm. Calculate:

(a) the equilibrium partial pressure of NO.

(b) K_p for $NO + NO_2 \rightleftharpoons N_2O_3$

87. In a vessel, two equilibria are simultaneously established at the same temperature as follows:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

$$N_2(g) + 2H_2(g) \rightleftharpoons N_2H_4(g)$$

Initially the vessel contains N_2 and H_2 in the molar ratio of 9 : 13. The equilibrium pressure is $7p_0$, in which pressure due to ammonia is p_0 and due to hydrogen is $2p_0$. Find the values of equilibrium constants (K_p) for both the reactions.

88. Two solids X and Y dissociate into gaseous products at a certain temperature as follows:

$$X(s) \rightleftharpoons A(g) + C(g) \text{ and}$$

$$Y(s) \rightleftharpoons B(g) + C(g).$$

At a given temperature, pressure over excess solid X is 40 mm and total pressure over solid Y is 60 mm. Calculate:

(a) the values of K_p for two reactions (in mm^2).

(b) the ratio of moles of A and B in the vapor state over a mixture of X and Y.

(c) the total pressure of gases over a mixture of X and Y.

89. When 1 mol of A (g) is introduced in a closed rigid 1 L vessel maintained at constant temperature, the following equilibria are established.

$$A(g) \rightleftharpoons B(g) + C(g) : K_{C1}$$

$$C(g) \rightleftharpoons D(g) + B(g) : K_{C2}$$

The pressure at equilibrium is twice the initial pressure. Calculate the value of $\frac{K_{C2}}{K_{C1}}$ if $\frac{[C]_{eq}}{[B]_{eq}} = \frac{1}{5}$

90. Solid NH_4I on rapid heating in a closed vessel at 357°C develops a constant pressure of 275 mm Hg due to partial decomposition of NH_4I into NH_3 and HI but the pressure gradually increases further (when the excess solid residue remains in the vessel) due to the dissociation of HI. Calculate the final pressure developed at equilibrium.

$$NH_4I(s) \rightleftharpoons NH_3(g) + HI(g)$$

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g);\ K_C = 0.065 \text{ at } 357°C$$

IONIC EQUILIBRIUM

91. 10 mL of 0.2 M H_2SO_4 is mixed with 20 mL of 0.2 M $Ba(OH)_2$ solution, the solution obtained is filtered and the obtained solution after filtering is reacted with some of 20 mL of 0.2 M CH_3COOH solution. Calculate pH of final solution. (Given $pK_{a(CH_3COOH)} = 4.74$)

92. Calculate the pH of a 0.15 M aqueous solution of $AlCl_3$. [Given: log 2 = 0.3, log 3 = 0.48.]

$$[Al(H_2O)_6]^{3+} + H_2O(l) \rightleftharpoons [Al(H_2O)_5OH]^{2+}(aq) + H_3O^+(aq),\ K_a = 1.5 \times 10^{-5}.$$

93. 50 mL of 0.1 M H_3PO_4 is titrated against 0.1 M NaOH. Calculate the pH when volume of NaOH added is

(i) 0 mL **(ii)** 25 mL **(iii)** 50 mL
(iv) 75 mL **(v)** 90 mL **(vi)** 100 mL
(vii) 125 mL **(viii)** 150 mL **(ix)** 200 mL

(Given: For H_3PO_4 $pK_{a1} = 3$, $pK_{a2} = 7$, $pK_{a3} = 11$.)

94. 2×10^{-4} mol of Mn^{2+} and Cu^{2+} each is present in 1 L solution of 10^{-3} M $HClO_4$, which is saturated with H_2S. Whether or not each of the ions will be precipitated? Given that concentration of H_2S in its saturated solution is 0.1 M. $K_{a,H_2S(overall)} = 10^{-21}$, $K_{sp(MnS)} = 2.5 \times 10^{-10}$ and $K_{sp(CuS)} = 8.5 \times 10^{-36}$.

95. Calculate the solubility of AgCN in a buffer solution of pH = 3. Given that $K_{sp(AgCN)} = 1.2 \times 10^{-15}$, $K_{a(HCN)} = 4.8 \times 10^{-10}$.

96. Calculate the solubility of MnS in a buffer of pH = 6. Given that for H_2S, $K_{a1} = 10^{-7}$ and $K_{a2} = 10^{-14}$ and solubility of MnS in water is 10^{-8} M.

97. Equal volumes of 0.02 M $AgNO_3$ and 0.02 M HCN was mixed. Calculate $[Ag^+]$ at equilibrium. Given $K_{a(HCN)} = 4 \times 10^{-10}$, $K_{sp(AgCN)} = 4 \times 10^{-16}$.

98. The equilibrium constants for amino acids are given in terms of successive ionization constants of the protonated form, for example, equilibrium constants for glycine (NH_2CH_2COOH) are $K_{a1} = 5 \times 10^{-3}$ M and $K_{a2} = 2 \times 10^{-10}$ M. What will be the pH at the isoelectric point for this amino acid and pH of 0.02 M protonated glycine in pure water respectively? [Take log 2 = 0.30]

99. Given:

$$Zn(OH)_2(s) \rightleftharpoons Zn(OH)_2(aq); K_1 = 10^{-6}$$

$$Zn(OH)_2(aq) \rightleftharpoons [Zn(OH)]^+ + OH^-(aq); K_2 = 10^{-7}$$

$$[Zn(OH)]^+(aq) \rightleftharpoons Zn^{2+} + OH^-(aq); K = 10^{-4}$$

$$[Zn(OH)_2](aq) + OH^- \rightleftharpoons [Zn(OH)_3]^-; K_4 = 10^3$$

$$[Zn(OH)_3]^-(aq) + OH^- \rightleftharpoons [Zn(OH)_4]^{2-}; K_5 = 10$$

Find out the negative of logarithm of the solubility of solid $Zn(OH)_2$ at 25°C at pH = 6. Consider that $Zn(OH)_2$ makes saturated solution at 25°C.

100. What is the solubility (in 10^{-4} mol L^{-1}) of TlN_3 in a solution prepared by shaking excess of TlN_3 and Tl_3PO_4.The solution produced contains 1 m mol of PO_4^{3-} per 200 mL solution. $K_{sp}(TlN_3) = 5.6875 \times 10^{-4}$.

ELECTROCHEMISTRY

101. The overall formation constant for the reaction of 6 mol of CN^- with cobalt(II) is 1×10^{19}. Calculate the formation constant for the reaction of 6 mol of CN^- with cobalt(III). Given that:

$$Co(CN)_6^{3-} + e^- \longrightarrow [Co(CN)_6]^{4-}; E^o = -0.83\ V$$

$$Co^{+3} + e^- \longrightarrow Co^{2+}; E^o = 1.82\ V$$

102. EMF diagram for iron is given as follows:

$$\underset{(Fe=+6)}{FeO_4^{2-}} \xrightarrow{E^o = +2.20\,V} \underset{(Fe=+3)}{Fe^{3+}} \xrightarrow{E^o = +0.77\,V}$$

$$\underset{(Fe=+2)}{Fe^{2+}} \xrightarrow{E^o = -0.445\,V} \underset{(Fe=0)}{Fe^0}$$

Determine the value of $E^o_{FeO_4^{2-}/Fe^{2+}}$.

103. The conductivity of a saturated aqueous solution of $Ag_2C_2O_4$ is 3.8×10^{-5} ohm^{-1} cm^{-1} at 25ºC. Determine the molar conductivity of oxalate ion. Given that, at 25ºC, conductivity of water is 6.2×10^{-6} ohm^{-1} cm^{-1}, molar conductivity of Ag^+ at infinite dilution is 62 ohm^{-1} cm^2 mol^{-1} and K_{sp} of $Ag_2C_2O_4$ is 1.1×10^{-11}?

104. In two vessels, each containing 500 mL water, 0.5 m mol of aniline ($K_b = 10^{-9}$) and 25 m mol of HCl are added separately. Two hydrogen electrodes are constructed using these solutions. Calculate the EMF of cell made by connecting them appropriately.

105. Consider the following cell at 25°C $Ag|AgBr(s), Br^-||AgCl(s), Cl^-|Ag$ at 25°C. The solubility product constants of AgBr and AgCl are respectively 5×10^{-13} and 1×10^{-10}. For what ratio of the concentrations of Br^- and Cl^- ions would the EMF of the cell be zero?

106. Dissociation constant for $[Ag(NH_3)_2]^+$ into Ag^+ and $2NH_3$ is 6×10^{-8}. Calculate $E°$ for the following half reaction,

$$Ag(NH_3)_2^+ + e^- \rightarrow Ag + 2NH_3$$

$$Ag^+ + e^- \rightarrow Ag;\ E° = 0.799\ V$$

107. In the acid base titration [H_3PO_4(0.1 M) + NaOH (0.1 M)], EMF of the solution is measured by coupling these electrodes with suitable reference electrode. When alkali is added pH of solution is in accordance with equation, $E_{cell} = E^o_{cell} + 0.059$ pH. For H_3PO_4, $K_{a1} = 10^{-3}$; $K_{a2} = 10^{-8}$; $K_{a3} = 10^{-13}$

What is the cell EMF at the second end point of the titration if E^o_{cell} at this stage is 1.3805 V.

108. A fuel cell uses CH_4 (g) and forms CO_3^{2-} at the anode. It is used to power a car with 80 A. For 0.96 h, how many liters of CH_4 (g) (STP) would be required? (V_m = 22.4 L mol^{-1}) (F = 96500). Assume 100% efficiency.

109. Small spherical ball of silver metal is used in jewellery having diameter 0.1 cm, is obtained by the electrolytic deposition. If the total number of balls in jewellery is 10,000, then calculate the applied amount of electricity in coulombs, which is used on the deposition on electrodes having entire surface 0.12 m^2. [Density of Ag = 10.5]

It is assumed that 3.5% electricity consumed as wastage during electrolysis and 60% of electrode body immersed in electrode. [Give your answer in multiple of 10^4.]

CHEMICAL KINETICS

110. For the reactions of I, II and III orders, $k_1 = k_2 = k_3$ when concentrations are expressed in mol L^{-1}. What will be the relation in k_1, k_2, k_3, if concentration are expressed in mol mL^{-1}?

111. For the reaction A → B, the rate law expression is $-\frac{d[A]}{dt} = k[A]^{1/2}$. If initial concentration of A is A_0. Calculate:

(a) integrated form of the rate expression.

(b) nature of plot of $[A]^{1/2}$ vs. time.

(c) half-life period.

112. The specific rate constant of the decomposition of N_2O_5 is 0.008 min^{-1}. The volume of O_2 collected after 20 min is 16 mL. Find the volume that would be collected at the end of reaction. NO_2 formed is dissolved in CCl_4.

113. A definite volume of H_2O_2 undergoing spontaneous decomposition required 22.8 cm^3 of standard permanganate solution for titration. After 10 and 20 min respectively the volumes of permanganate required were 13.8 and 8.25 cm^3.

(a) Find order of reaction. How may the result be explained?

(b) Calculate the time required for the decomposition to be half completed.

(c) Calculate the fraction of H_2O_2 decomposed after 25 min.

114. At 100º C, the gaseous reaction A → 2B + C was observed to be of first order. On starting with pure A it is found that at the end of 10 min the total pressure of system is 176 mm Hg and after a long time 270 mm Hg. From these data find

(a) initial pressure of A.

(b) the pressure of A at the end of 10 min.

(c) the specific rate of reaction.

(d) the half-life period of the reaction.

115. For a reversible first-order reaction $A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$; $k_1 = 10^{-2}$ s^{-1} and $[B]_{eq}/[A]_{eq} = 4$. If $[A]_0 = 0.01$ mol L^{-1} and $[B]_0 = 0$, what will be the concentration of B after 30 s?

116. If a reaction A → Products, the concentrations of reactant A are C_0, aC_0, a^2C_0, a^3C_0, …. After time interval 0, t, $2t$, $3t$, ….. where a is a constant. Given $0 < a < 1$. Show that the reaction is of first order. Also find out the relation between k, a and t.

117. For the reaction given below, rate constant for disappearance of A is 7.48×10^{-3} s^{-1}. Calculate the time required for the total pressure in a system containing A at an initial pressure of 0.1 atm that rise to 0.145 atm and also find the total pressure after 100 s.

$$2A(g) \rightarrow 4B(g) + C(g)$$

118. The reaction A(aq) → B(aq) + C(aq) is monitored by measuring optical rotation of reaction mixture at different time interval. The species A, B and C are optically active with specific rotations 20°, 30° and –40° respectively. Starting with pure A, if the value of optical rotation was found to be 2.5° after 6.93 min and optical rotation was –5° after infinite time. Find the rate constant for first order conversion of A into B and C.

119. The decomposition of a compound P, at temperature T according to the equation

$$2P(g) \rightarrow 4Q(g) + R(g) + S(l)$$

is the first order reaction. After 30 min from the start of decomposition in a closed vessel, the total pressure developed is found to be 317 mm Hg and after a long period of time and total pressure observed to be 617 mm Hg. Calculate the total pressure of the vessel after 75 min, if volume of liquid S is supposed to be negligible. Also calculate the time fraction $t_{7/8}$.

Given: Vapor pressure of S(l) at temperature $T = 32.5$ mm Hg.

120. A certain reactant B^{n+} is getting converted to $B^{(n+4)}$ in solution. The rate constant of this reaction is measured by titrating a volume of the solution with a reducing reagent which only reacts with B^{n+} and $B^{(n+4)+}$. In this process, it converts B^{n+} to $B^{(n-2)+}$ and $B^{(n+4)+}$ to $B^{(n-1)+}$. At $t = 0$, the volume of the reagent consumed is 25 mL and $t = 10$ min, the volume used up is 32 mL. Calculate the rate constant of the conversion of B^{n+} to $B^{(n+4)+}$ assuming it to be a first order reaction.

121. For the mechanism $A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C;\ C \xrightarrow{k_3} D$

(a) Derive the rate law using the steady-state approximation to eliminate the concentration of C.

(b) Assuming that $k_3 \ll k_2$, express the pre-exponential factor A and E_a for the apparent second-order rate constant in terms of A_1, A_2 and A_3 and E_{a1}, E_{a2} and E_{a3} for the three steps.

SURFACE CHEMISTRY

122. The pressure of the gas was found to decrease from 720 to 480 mm. When 5 g sample of activated charcoal was kept in a flask of one liter capacity maintained at 27ºC and the density of charcoal is 1.25 g mL^{-1}. What is the volume of gas adsorbed per gram of charcoal at 480 mm?

123. Coagulation value of the electrolytes $AlCl_3$ and NaCl for As_2S_3 sol are 0.093 and 52 respectively. How many times $AlCl_3$ has greater coagulating power than NaCl?

124. Graph between log x/m and log p is straight line inclined at an angle of 45º. When pressure is 0.5 atm and ln$k$ = 0.693, what will be the amount of solute adsorbed per gram of adsorbent?

125. The density of gold is 19 g cm^{-3}. If 1.9×10^{-4} g of gold is dispersed in one liter of water to give a sol having spherical gold particles of radius 10 nm, what will be number of gold particles per mm^3 of the sol?

126. 100 mL of a colloidal solution is completely precipitated by addition of 0.5 mL of 1 M NaCl solution. Calculate the coagulation value of NaCl.

127. On addition of the 1 mL solution of 10% NaCl to 10 mL gold sol in the presence of 0.00399 g of starch, calculate the gold number.

128. Coagulation experiment, 5 mL of As_2S_3 is mixed with distilled water and 0.01 M solution of an electrolyte AB so that total volume is 10 mL. It was found that all solution containing more than 5 mL of AB coagulates within 5 min. What is the flocculation value of AB for As_2S_3 sol?

NUCLEAR CHEMISTRY

129. A sample of radioactive ^{133}I gave with Geiger counter 3150 counts per minute at a certain time and 3055 counts per minute exactly one hour later. Calculate the half-life period of ^{133}I.

130. For ^{24}Na, $t_{1/2} = 14.8$ h. In what period of time will a sample of this substance lose 90% of its radioactive intensity?

131. ^{90}Y has a half-life of 64 h and ^{90}Sr, 28 years. ^{90}Sr decays to ^{90}Y by β-emission. What will be the amount of ^{90}Y in equilibrium with 1 g of ^{90}Sr?

132. A sample of U^{238} (half-life = 4.5×10^9 year) ore is found to contain 23.8 g of U^{238} and 20.6 g of Pb^{206}. Calculate the age of the ore.

133. Consider the following reaction:

$$^2H_1 + {}^2H_1 = {}^4He_2 + Q$$

Mass of the deuterium atom = 2.0414 u; Mass of the helium atom = 4.0024 u. Find ‘Q’.

134. The binding energy per nucleon for $^2H_1$ and $^4He_2$ are 1.1 MeV and 7.0 MeV respectively. Find the energy released when the two deuterons fuse to form a helium nucleus.

ANSWER KEY

Mole Concept–I

1. 2.04×10^{-21} atm **2.** 47.31% **3.** 0.26

4. $CH_4 = 4.5$ mL, $C_2H_4 = 4$ mL, $CO_2 = 1.5$ mL

5. $FeO = 20.25\%$, $Fe_3O_4 = 79.75\%$

6. $NaCl = 4.21\%$, $NaBr = 23.1\%$

7. 1041.67 kg m^{-3} **8.** 1.09375 kg

Mole Concept–II

9. 92.4% **10.** 2.54 g **11.** 13.05%

12. % of $K_2Cr_2O_7 = 14.64\%$; % of $KMnO_4 = 85.36\%$

13. 4.669 L **14.** 0.5 g **15.** 0.06

16. 50% **17.** 78.22%

18. $SCN^- + 3I_2 + 4H_2O \rightarrow SO_4^{2-} + HCN + 7H^+ + 6I^-$; 25%

Liquid and Gaseous State

19. 5 **20.** 6 **21.** 3 **22.** 4

23. 0.199 **24.** 10000 K **25.** 1.7×10^{-8}

26. **(a)** 1.34×10^{-22} cm^3 **(b)** 80.71 cm^3 **(c)** 242.13 cm^3

27. **(a)** $n = \dfrac{-T}{100} + 5$ **(b)** $V = \dfrac{-RT^2}{100} + 5RT$

(c) 51.3125 L

Solid State

28. **(a)** 2.878 Å **(b)** 12 **(c)** 19.4 g cm^{-3} **(d)** 0.7405

29. 0.414 r, 79.3%

30. **(a)** 4.5 Å **(b)** 5.2Å **(c)** 8

(d) 6 **(e)** 0.92 g cm^{-3}

31. 6.02×10^{18} mol^{-1}

32. **(a)** 3.90 **(b)** 0.120 g cm^{-3}

33. 2.376%

Atomic Structure

34. (3) **35.** (6) **36.** (8)

37. $Z = 3; n = 6$ **38.** 12 **39.** 325 kJ mol^{-1}

40. **(a)** $r_0 = 2a_0$ **(b)** 6.626×10^{-35} m

41. 13225 **42.** **(a)** 6 **(b)** 96 **43.** 26

44. $n = 1$ to $n = 2$; 4.423×10^4 m s^{-1}.

45. 186 kJ **46.** 498.22 kJ mol^{-1}

47. 1212 Å, 1022 Å, 5545 Å

48. **(a)** 5 **(b)** 23.9×10^{-19} J

(c) 36.5 Å **(d)** 5.45×10^{-10} erg

49. 2.351 Å **50.** **(a)** 9 **(b)** 25 **51.** 2.06

Chemical Bonding

53. **(a)** 3.50 Å **(b)** 6.06 Å **(c)** 7.0 Å

55. 3.23×10^{-10} esu **56.** 11.65%

57. **(a)** each sp^2 hybridized **(b)** $\alpha = \beta = 120°$

59. 25%

Chemical Energetics

61. –338.4 kcal **62.** $\Delta T = \dfrac{9}{3R}$ **63.** 12.36 cm

64. **(a)** $w_A = -3458$ J; **(b)** $\Delta E_B = 0$;

(c) $q_B = -3457$ J

(d) $q_A = 27.458$ kJ; $\Delta E_A = 24$ kJ

65. –88 kJ **66.** 6.86 min

67. **(a)** $T_1 = 243.60$ K, $T_2 = 2436.0$ K

(b) in path CA $w = +1122.02$ cal, $\Delta E = 0$, $q = w$ in path AB $w = -4384.9$ cal, $\Delta E = +6577.2$ cal, $q = 10962.1$ cal in path BC $w = 0$, $q = \Delta E = -6577.2$

68. –211.62 J

69. **(a)** $\Delta S_{sys} = 0$; $\Delta S_{surr} = 0$; $\Delta S_{total} = 0$

(b) $\Delta S_{sys} = 0.957$ J K^{-1}; $\Delta S_{surr} = 0$; $\Delta S_{total} = 0.957$ J K^{-1}

(c) $\Delta S_{sys} = 3.81$ J K^{-1}; $\Delta S_{surr} = 0$; $\Delta S_{total} = 3.81$ J K^{-1}

70. 3 kcal **71.** 9 kJ **72.** 1 kJ **73.** 24.7 kJ

74. 122 kcal mol^{-1} **75.** $\Delta U = 10$ J and $\Delta H = 990$ J

76. $w = -pV$; $q = pV$

Solutions

77. 36 **78.** 352.98 g

79. **(a)** 210.65 **(b)** 62.35%

80. $[Co(NH_3)_5Cl]Cl_2$ **81.** 20.11%

82. ΔH_V at 80 K is 1659.1 calorie;
$\Delta H_V = R\,[2.303 \times 313.7 + 1.40655\,T]$

83. $l = 5$ **84.** 0.3 **85.** 2978.6 kJ mol^{-1}.

Chemical Equilibrium

86. (a) 1.05 atm, **(b)** 3.43 atm

87. $K_{p_1} = \dfrac{1}{20\,p_0^2}$, $K_{p_2} = \dfrac{3}{20\,p_0^2}$

88. **(a)** 400 mm^2, 900 mm^2 **(b)** 4 : 9 **(c)** 72.15 mm g

89. 4 **90.** 337 mm Hg

Ionic Equilibrium

91. 8.82 **92.** pH = 2.82

93. **(a)** 2 **(b)** 3 **(c)** 5 **(d)** 7 **(e)** 7.6
(f) 9 **(g)** 11 **(h)** 11.7 **(i)** 12.3

94. CuS will be precipitated

95. $S = 5 \times 10^{-5}$ **96.** 3.32×10^{-4} M **97.** 10^{-4}

98. 2 **99.** 1 **100.** 1.75×10^{-2} mol L^{-1}

Electrochemistry

101. 5.64×10^{35} **102.** 1.84 V

103. 103 Ω^{-1} cm^2 mol^{-1} **104.** 0.395 V

105. $[Br^-] : [Cl^-] = 1 : 200$

106. 0.373 V **107.** 2 V **108.** 8 L **109.** 5

Chemical Kinetics

110. $k_1 = 10^{-3}; k_2 = 10^{-6}\,k_3$

111. **(a)** $k_t = 2\left(A_0^{1/2} - A_{1/2}\right)$

(b) linear with negative slope

(c) $(t)^{1/2} = \dfrac{V_2(V_2 - 1)}{k}\;A_0^{1/2}$

112. 108.48 mL

113. **(a)** 1 **(b)** 13.71 min **(c)** 0.715

114. **(a)** 90 mm **(b)** 47 mm
(c) 0.065 min^{-1} **(d)** 10.677

115. 0.0025 m **116.** $k = \dfrac{2.303}{t}\log\dfrac{1}{a}$

117. 0.180 atm, 47.69 s **118.** 0.1 min^{-1}

119. $p_t = 379.55$ mm Hg, $t_{7/8} = 399.96$ min

120. 0.0207 min^{-1}

121. **(a)** $\dfrac{d(D)}{dt} = \dfrac{k_1 k_3 (A)(B)}{k_2 + k_3}$;

(b) $E_a = E_{a1} + E_{a3} - E_{a2}; A = \dfrac{A_1 A_3}{A_2}$

Surface Chemistry

122. 100.08 mL **123.** 560 **124.** 1

125. 2.4×10^9 **126.** 5 **127.** 4 **128.** 5

Nuclear Chemistry

129. 22.63 years **130.** 49.17 h

131. 2.609×10^{-4} g **132.** 4.5×10^9 years

133. 24 **134.** 23.6 MeV

JEE (ADVANCED) 2018
PAPER I (CHEMISTRY)

SECTION 1

- This section contains **SIX (06)** questions.
- Each question has **FOUR** options for correct answer(s). **ONE OR MORE THAN ONE** of these four option(s) is (are) correct option(s).

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1. The compound(s) which generate(s) N_2 gas upon thermal decomposition below 300°C is (are)
(A) NH_4NO_3 (B) $(NH_4)_2Cr_2O_7$ (C) $Ba(N_3)_2$ (D) Mg_3N_2

Solution

(B) (C) Ammonium salts decompose quite readily on heating. If the anion is more oxidizing (e.g. $NO_3^-, Cr_2O_7^{2-}$) then NH_4^+ gets oxidized to N_2 or N_2O.

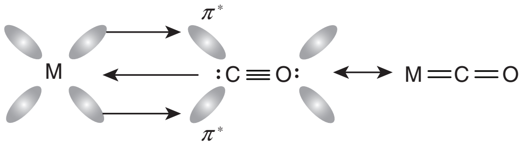
$$NH_4NO_3 \xrightarrow{\text{Heat}} N_2O + 2H_2O$$
$$(NH_4)_2Cr_2O_7 \xrightarrow{\text{Heat}} N_2 + 4H_2O + Cr_2O_3$$
$$Ba(N_3)_2 \xrightarrow{\text{Heat}} Ba + 3N_2$$

Mg_3N_2 is an ionic compound, therefore, will not decompose at 300°C.

2. The correct statement(s) regarding the binary transition metal carbonyl compounds is (are) (Atomic numbers: Fe = 26, Ni = 28)
(A) Total number of valence shell electrons at metal centre in $Fe(CO)_5$ or $Ni(CO)_4$ is 16.
(B) These are predominantly low spin in nature.
(C) Metal–carbon bond strengthens when the oxidation state of the metal is lowered.
(D) The carbonyl C—O bond weakens when the oxidation state of the metal is increased.

Solution

(B) (C) Option (A): Incorrect. Total number of valence shell electrons in $Fe(CO)_5$ $[8 + 5 \times 2 = 18]$ and $Ni(CO)_4$ $[10 + 4 \times 2 = 18]$ is 18.
Option (B): Correct. CO being a strong field ligand cause pairing of electrons. Hence, both the complexes formed are low spin in nature.
Option (C): Correct. CO ligand not only donates the lone pair of electrons to the central atom but also accept the electron cloud from the central atom in their low-lying vacant orbitals. This kind of back donation is known as 'synergic effect' or 'synergic bonding. In case of CO, the back donation to the π^* orbital of central atom may be depicted as:



Greater the electron density on the metal atom, that is, lower the oxidation state of the metal, greater will be the back donation hence stronger will be the M—C bond.
Option (D): Incorrect. When the oxidation state of metal increases its tendency to accept the electrons from C of CO increases but tendency to donate the electrons from M to C decreases consequently M—C bond strength decreases and C—O bond strength increases.

3. Based on the compounds of group 15 elements, the correct statement(s) is (are)

(A) Bi_2O_5 is more basic than N_2O_5.
(B) NF_3 is more covalent than BiF_3.
(C) PH_3 boils at lower temperature than NH_3.
(D) The N—N single bond is stronger than the P—P single bond.

Solution

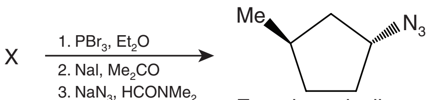
(A) (B) (C) Option (A): Correct. The basicity of oxides usually increases on descending a group. Therefore, Bi_2O_5 is more basic than N_2O_5.

Option (B): Correct. Covalent nature of a molecule depends on the electronegativity difference between bonded atoms.

Option (C): Correct. Boiling point of NH_3 is more than that of PH_3 due to hydrogen bonding.

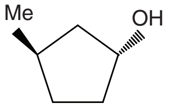
Option (D): Incorrect. P—P single bond is stronger than N—N single bond. This is due to the fact that N is small in size, due to smaller size of atoms lone pair of repulsion will be more.

4. In the following reaction sequence, the correct structure(s) of **X** is (are)

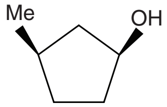


Enantiomerically pure

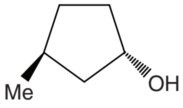
(A)



(B)



(C)



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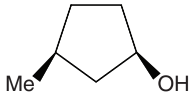
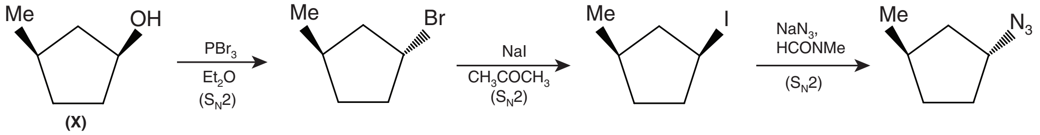


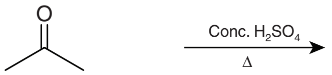
Solution

(B)

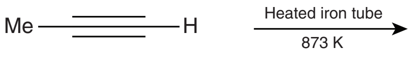


5. The reaction(s) leading to the formation of 1, 3, 5-trimethylbenzene is (are)

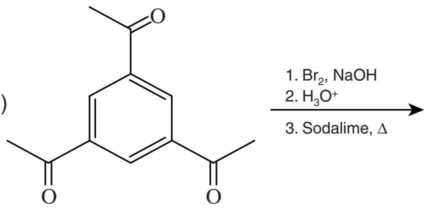
(A)



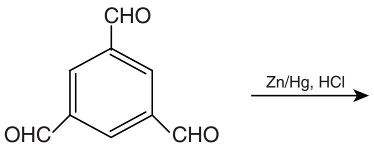
(B)



(C)

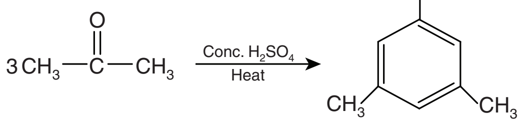


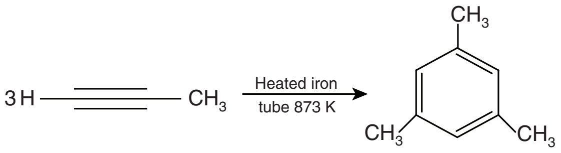
(D)

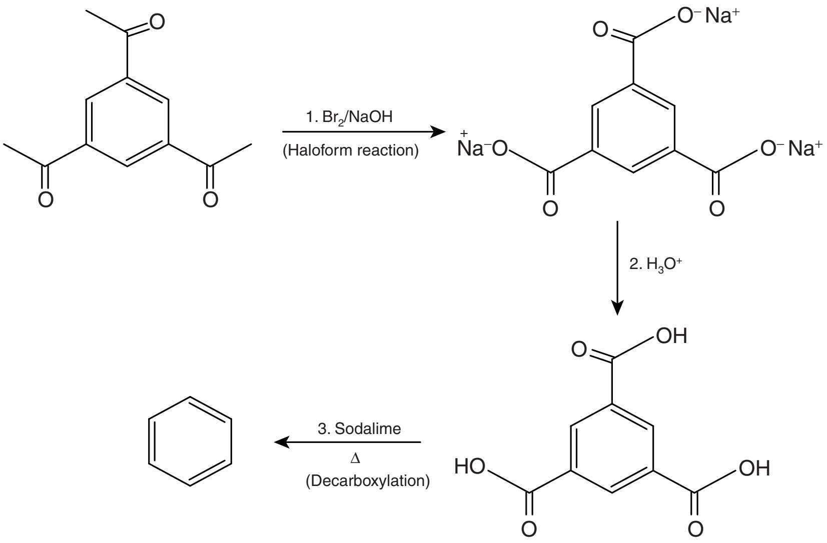


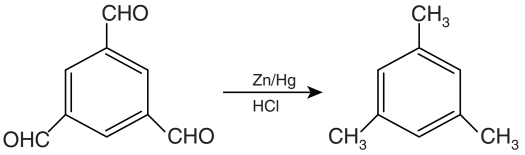
Solution

(A) (B) (D)

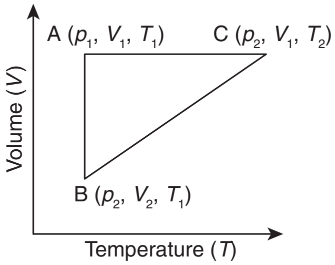








6. A reversible cyclic process for an ideal gas is shown below. Here p, V, and T are pressure, volume and temperature, respectively. The thermodynamic parameters q, w, H and U are heat, work, enthalpy and internal energy, respectively.



The correct option(s) is (are)

(A) $q_{AC} = \Delta U_{BC}$ and $w_{AB} = p_2(V_2 - V_1)$

(B) $w_{BC} = p_2(V_2 - V_1)$ and $q_{BC} = \Delta H_{AC}$

(C) $\Delta H_{CA} < \Delta U_{CA}$ and $q_{AC} = \Delta U_{BC}$

(D) $q_{BC} = \Delta H_{AC}$ and $\Delta H_{CA} > \Delta U_{CA}$

Solution

(B) (C) We know $\Delta U = q + w$ and $w = -p\Delta V$

In the above figure, A-C is isochoric, A-B is isothermal and B-C is isobaric process. Therefore, for an isochoric process AC, we have

$$q_{\text{AC}} = \Delta U_{\text{AC}} = nC_{V,\text{m}}(T_2 - T_1) = \Delta U_{\text{BC}}$$

For an isobaric process BC, we have

$$q_{\text{BC}} = \Delta H_{\text{BC}} = nC_{p,\text{m}}(T_2 - T_1) = \Delta H_{\text{AC}}$$
$$w_{\text{BC}} = -p_2(V_1 - V_2) = p_2(V_2 - V_1)$$
$$\Delta H_{\text{CA}} = nC_{p,\text{m}}(T_1 - T_2) \text{ and } \Delta U_{\text{CA}} = nC_{V,\text{m}}(T_1 - T_2)$$

Since, $T_2 > T_1$, therefore, ΔH_{CA} and ΔU_{CA} are negative.

$$\Delta H_{\text{CA}} = \Delta U_{\text{CA}} + V\Delta p$$

As $\Delta p < 0$, therefore, $\Delta H_{\text{CA}} < \Delta U_{\text{CA}}$.

SECTION 2

- This section contains **EIGHT (08)** questions. The answer to each question is a **NUMERICAL VALUE**.

---

7. Among the species given below, the total number of diamagnetic species is _______.
H atom, NO_2 monomer, O_2^- (superoxide), dimeric sulphur in vapor phase, Mn_3O_4, $(NH_4)_2[FeCl_4]$, $(NH_4)_2[NiCl_4]$, K_2MnO_4, K_2CrO_4

Solution

(1) The paramagnetic species are H atom, NO_2 monomer, O_2^- (superoxide), dimeric sulphur in vapor phase, Mn_3O_4, $(NH_4)_2[FeCl_4]$, $(NH_4)_2[NiCl_4]$ and K_2MnO_4.
The diamagnetic species is K_2CrO_4.

8. The ammonia prepared by treating ammonium sulphate with calcium hydroxide is completely used by $NiCl_2\cdot 6H_2O$ to form a stable coordination compound. Assume that both the reactions are 100% complete. If 1584 g of ammonium sulphate and 952 g of $NiCl_2\cdot 6H_2O$ are used in the preparation, the combined weight (in grams) of gypsum and the nickel–ammonia coordination compound thus produced is _______.
(Atomic weights in g mol^{-1}: H = 1, N = 14, O = 16, S = 32, Cl = 35.5, Ca = 40, Ni = 59)

Solution

The reactions involved are as follows:

$$(NH_4)_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4\cdot 2H_2O + 2NH_3$$

$$NiCl_2\cdot 6H_2O + 6NH_3 \rightarrow [Ni(NH_3)_6]Cl_2 + 6H_2O$$

From the above reactions we can see that
132 g of $(NH_4)_2SO_4$ will produce 172 g of gypsum

1584 g of $(NH_4)_2SO_4$ will produce $\frac{172}{132}\times 1584 = 2064$ g of gypsum

Therefore, number of moles of gypsum produced $\frac{2064}{172} = 12$ mol

238 g of $NiCl_4 \cdot 6H_2O$ will produce 314 g of Ni-complex

952 g of $NiCl_4 \cdot 6H_2O$ will produce $\frac{314}{238} \times 952 = 1256\,g$ of Ni-complex

Therefore, number of moles of Ni-complex produced $\frac{1256}{314} = 4\,mol$

So, total mass of products is 12×172 (gypsum) $+ 4 \times 232$ ($[Ni(NH_3)_6]Cl_2$) = 2992 g

9. Consider an ionic solid **MX** with NaCl structure. Construct a new structure (**Z**) whose unit cell is constructed from the unit cell of **MX** following the sequential instructions given below. Neglect the charge balance.

(i) Remove all the anions (**X**) except the central one
(ii) Replace all the face centered cations (**M**) by anions (**X**)
(iii) Remove all the corner cations (**M**)
(iv) Replace the central anion (**X**) with cation (**M**)

The value of $\left(\frac{\text{number of anions}}{\text{number of cations}}\right)$ in $\boldsymbol{Z}$ is _______.

Solution

(3) Given that MX is an ionic solid having NaCl type structure having ccp. So, the anion X^- occupies all octahedral voids. The changes (i)-(iv) cause the following effects:

(i) No. of anions left = 1
(ii) No. of anions added by replacing face centered cations M = 3; No. of cations left = 1
(iii) No. of cations left = 0
(iv) No. of cations added = 1; No. of anions left = 3

Finally, the unit cell contains 1 cation and 3 anions. So,

The value of $\left(\frac{\text{number of anions}}{\text{number of cations}}\right)$ in $\boldsymbol{Z}$ is 3.

10. For the electrochemical cell,

$$Mg(s) \mid Mg^{2+} (aq, 1\ M) \parallel Cu^{2+} (aq, 1\ M) \mid Cu(s)$$

the standard emf of the cell is 2.70 V at 300 K. When the concentration of Mg^{2+} is changed to x M, the cell potential changes to 2.67 V at 300 K. The value of x is _______.

(Given, $\frac{F}{R} = 11500\ K\ V^{-1}$, where F is the Faraday constant and R is the gas constant, ln (10) = 2.30)

Solution

(10) The cell reaction is

$$Mg(s) + Cu^{2+}(aq, 1\ M) \rightarrow Mg^{2+}(aq, x\ M) + Cu(s)$$

$$E_{cell} = E^{o}_{cell} - 2.303 \times \frac{RT}{2F} \log \frac{[Mg^{2+}]}{[Cu^{2+}]}$$

$$2.67 = 2.70 - 2.303 \times \frac{300}{2 \times 11500} \log(x)$$

$$0.03 = \frac{2.303 \times 3}{115 \times 2} \log x \Rightarrow \log x = 1 \Rightarrow x = 10$$

11. A closed tank has two compartments **A** and **B**, both filled with oxygen (assumed to be ideal gas). The partition separating the two compartments is fixed and is a perfect heat insulator (Figure 1). If the old partition is replaced by a new partition which can slide and conduct heat but does **NOT** allow the gas to leak across (Figure 2), the volume (in m^3) of the compartment **A** after the system attains equilibrium is ______.

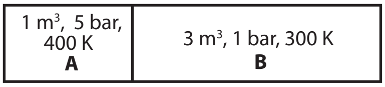


Figure 1

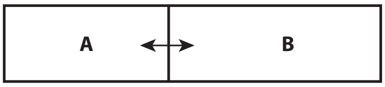


Figure 2

Solution

(2.22) Using $pV = nRT$, we have

In Figure 1,

$$n_A = \frac{p_A V_A}{RT} = \frac{5}{400R} \text{ and } n_B = \frac{p_B V_B}{RT} = \frac{1}{100R}$$

In Figure 2, after equilibrium is attained, we have

$$p_A = p_B \text{ and } T_A = T_B = T, \text{ so}$$

$$\frac{n_A RT}{V_A} = \frac{n_B RT}{V_B} \Rightarrow \frac{5}{400R \cdot V_A} = \frac{1}{100R \cdot V_B}$$

$$\Rightarrow 4V_A = 5V_B$$

Now, $$V_A + V_B = 4 \text{ m}^3, \text{ so } V_A + \frac{4}{5}V_A = 4 \Rightarrow V_A = \frac{20}{9} = 2.22 \text{ m}^3$$

12. Liquids **A** and **B** form ideal solution over the entire range of composition. At temperature T, equimolar binary solution of liquids **A** and **B** has vapor pressure 45 torr. At the same temperature, a new solution of **A** and **B** having mole fractions x_A and x_B, respectively, has vapor pressure of 22.5 torr. The value of x_A/x_B in the new solution is

(Given that the vapor pressure of pure liquid **A** is 20 torr at temperature T)

Solution

(19) $$p^{\circ}_A x_A + p^{\circ}_B x_B = p_T = 45$$

For equimolar binary solution, $x_A = x_B = 0.5$, so

$$20 \times 0.5 + p_B \times 0.5 = 45 \Rightarrow 70 \text{ torr}$$

For the new solution,

$$p^{\circ}_B + (p^{\circ}_A - p^{\circ}_B)x_A = 22.5 \Rightarrow 70 + (20 - 70)x_A \Rightarrow 22.5 \Rightarrow x_A = 47.5/50$$

Now, $$\frac{x_A}{x_B} = \frac{x_A}{1 - x_A} = \frac{47.5/50}{1-(47.5/50)} = \frac{47.5}{2.5} = 19$$

13. The solubility of a salt of weak acid (AB) at pH 3 is Y × 10^{-3} mol L^{-1}. The value of Y is ______.

(Given that the value of solubility product of AB (K_{sp}) = 2×10^{-10} and the value of ionization constant of HB (K_a) = 1×10^{-8})

Solution

(4.47) The reactions are

$$\underset{}{\mathrm{AB(s)}} \rightleftharpoons \underset{S}{\mathrm{A^+(aq)}} + \underset{S-x}{\mathrm{B^-(aq)}}$$

$$\underset{S-x}{\mathrm{B^-(aq)}} + \underset{10^{-3}}{\mathrm{H^+(aq)}} \rightleftharpoons \mathrm{HB}$$

Now, for HB,

$$K_{\mathrm{a}} = \frac{[\mathrm{H^+}][\mathrm{B^-}]}{[\mathrm{HB}]} \Rightarrow \frac{(s-x)\times 10^{-3}}{x} = 10^{-8}$$

$$\Rightarrow s - x = x \times 10^{-5}$$

$$K_{\mathrm{sp}} = [\mathrm{A^+}][\mathrm{B^-}] = S(S-x) = 2\times 10^{-10}$$

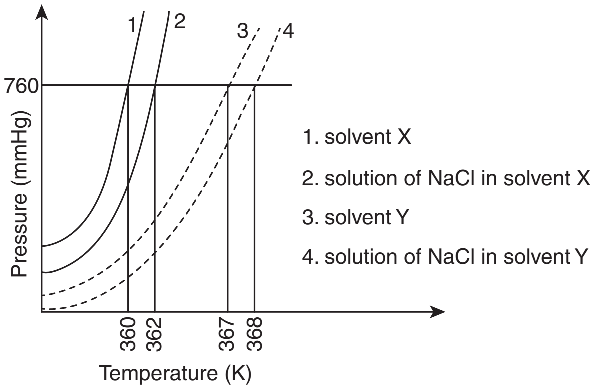
Putting $Sx = 2\times 10^{-5}$ in $S^2 - Sx - 2\times 10^{-10} = 0$, we get

$$S \quad \sqrt{(2\times\ 10^{-5})} = 4.47\times 10^{-3}\ \mathrm{M}$$

Alternate solution

$$S = \sqrt{K_{\mathrm{sp}}\left(\frac{[\mathrm{H^+}]}{K_{\mathrm{a}}}+1\right)} = \sqrt{20\times 10^{-10}\left(\frac{10^{-3}}{10^{-8}}+1\right)} \quad \sqrt{(2\times\ 10^{-5})} = 4.47\times 10^{-3}\ \mathrm{M}$$

14. The plot given below shows $p - T$ curves (where p is the pressure and T is the temperature) for two solvents **X** and **Y** and isomolal solutions of NaCl in these solvents. NaCl completely dissociates in both the solvents.



On addition of equal number of moles of a non–volatile solute **S** in equal amount (in kg) of these solvents, the elevation of boiling point of solvent **X** is three times that of solvent **Y**. Solute S is known to undergo dimerization in these solvents. If the degree of dimerization is 0.7 in solvent **Y**, the degree of dimerization in solvent **X** is

Solution

(0.05) For solvent X, $\Delta T_{\mathrm{bX}} = K_{\mathrm{bX}}\, m \Rightarrow 2 = 2K_{\mathrm{bX}}\, m$ (1)

For solvent Y, $\Delta T_{\mathrm{bY}} = K_{\mathrm{bY}}\, m \Rightarrow 1 = 2K_{\mathrm{bY}}\, m$ (2)

Dividing Eq. (1) by Eq. (2), we get

$$\frac{K_{\mathrm{bX}}}{K_{\mathrm{bY}}} = 2$$

After adding solute S, molality is the same for both solutions. So, we have

For solvent X, van’t Hoff factor $i = 1 - \dfrac{\alpha}{2}$

$$\Delta T_{\text{bX}} = iK_{\text{bX}}\, m = \left(1 - \frac{\alpha}{2}\right) K_{\text{bX}}\, m \tag{3}$$

For solvent Y, van’t Hoff factor $i = 1 - \dfrac{0.7}{2} = \dfrac{1.3}{2}$

$$\Delta T_{\text{bY}} = iK_{\text{bY}}\, m \Rightarrow \left(\frac{1.3}{2}\right) K_{\text{bY}}\, m \tag{4}$$

Given that $\Delta T_{\text{bX}} = 3\Delta T_{\text{bY}}$. Dividing Eq. (3)/(4), we have

$$\frac{\Delta T_{\text{bX}}}{\Delta T_{\text{bY}}} = \frac{\left(1 - \frac{\alpha}{2}\right) K_{\text{bX}}\, m}{\left(\frac{1.3}{2}\right) K_{\text{bY}}\, m} \Rightarrow \frac{1}{3} = \frac{2(2-\alpha)}{1.3} \Rightarrow \alpha = 0.05$$

SECTION 3

- This section contains **TWO (02)** paragraphs. Based on each paragraph, there are **TWO (02)** questions.
- Each question has **FOUR** options. **ONLY ONE** of these four options corresponds to the correct answer.

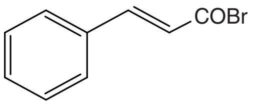
PARAGRAPH “X”

Treatment of benzene with CO/HCl in the presence of anhydrous $AlCl_3$/CuCl followed by reaction with Ac_2O/NaOAc gives compound **X** as the major product. Compound **X** upon reaction with Br_2/Na_2CO_3, followed by heating at 473 K with moist KOH furnishes **Y** as the major product. Reaction of **X** with H_2/Pd-C, followed by H_3PO_4 treatment gives **Z** as the major product.

(*There are two questions based on PARAGRAPH “X”, the question given below is one of them*)

15. The compound **Y** is

(A)



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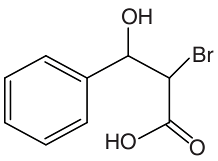

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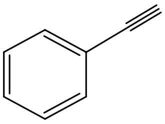

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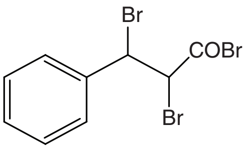
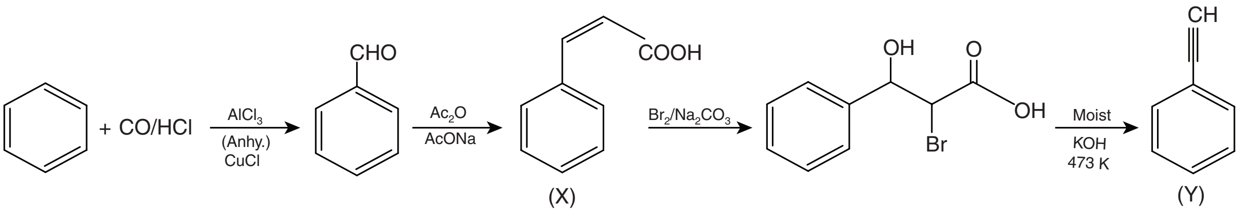


Solution

(C)



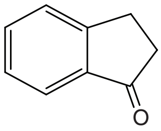
PARAGRAPH "X"

Treatment of benzene with CO/HCl in the presence of anhydrous $AlCl_3$/CuCl followed by reaction with Ac_2O/NaOAc gives compound **X** as the major product. Compound **X** upon reaction with Br_2/Na_2CO_3, followed by heating at 473 K with moist KOH furnishes **Y** as the major product. Reaction of **X** with H_2/Pd-C, followed by H_3PO_4 treatment gives **Z** as the major product.

(*There are two questions based on PARAGRAPH "X", the question given below is one of them*)

16. The compound **Z** is

(A)



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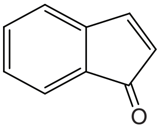

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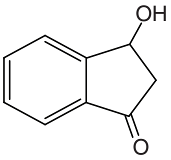

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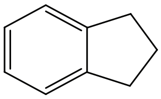
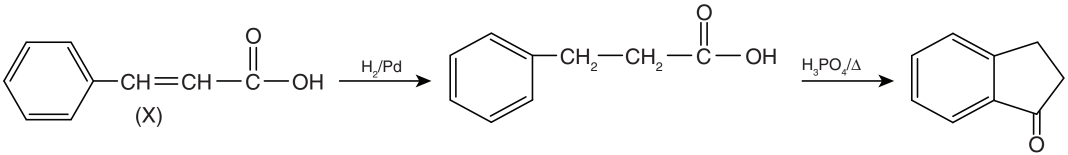


Solution

(A)



(X)

(Z)

PARAGRAPH "A"

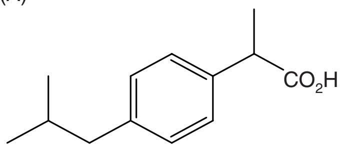
An organic acid **P** ($C_{11}H_{12}O_2$) can easily be oxidized to a dibasic acid which reacts with ethylene glycol to produce a polymer dacron. Upon ozonolysis, **P** gives an aliphatic ketone as one of the products. **P** undergoes the following reaction sequences to furnish **R** *via* **Q**. The compound **P** also undergoes another set of reactions to produce **S**.

$$\mathbf{S} \xleftarrow[\substack{\text{4. } CHCl_3,\ KOH,\ \Delta \\ \text{5. } H_2/Pd\text{-}C}]{\substack{\text{1. } H_2/Pd\text{-}C \\ \text{2. } NH_3/\Delta \\ \text{3. } Br_2/NaOH}} \mathbf{P} \xrightarrow[\substack{\text{3. } MeMgBr,\ CdCl_2 \\ \text{4. } NaBH_4}]{\substack{\text{1. } H_2/Pd\text{-}C \\ \text{2. } SOCl_2}} \mathbf{Q} \xrightarrow[\substack{\text{3. } CO_2 \text{ (dry ice)} \\ \text{4. } H_3O^+}]{\substack{\text{1. } HCl \\ \text{2. } Mg/Et_2O}} \mathbf{R}$$

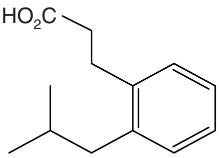
(*There are two questions based on PARAGRAPH "A", the question given below is one of them*)

17. The compound **R** is

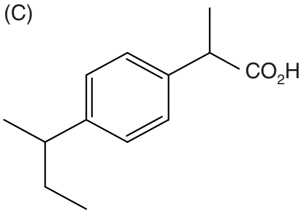
(A)



(B)



(C)



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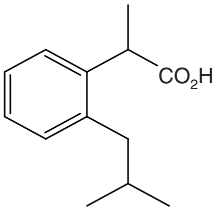
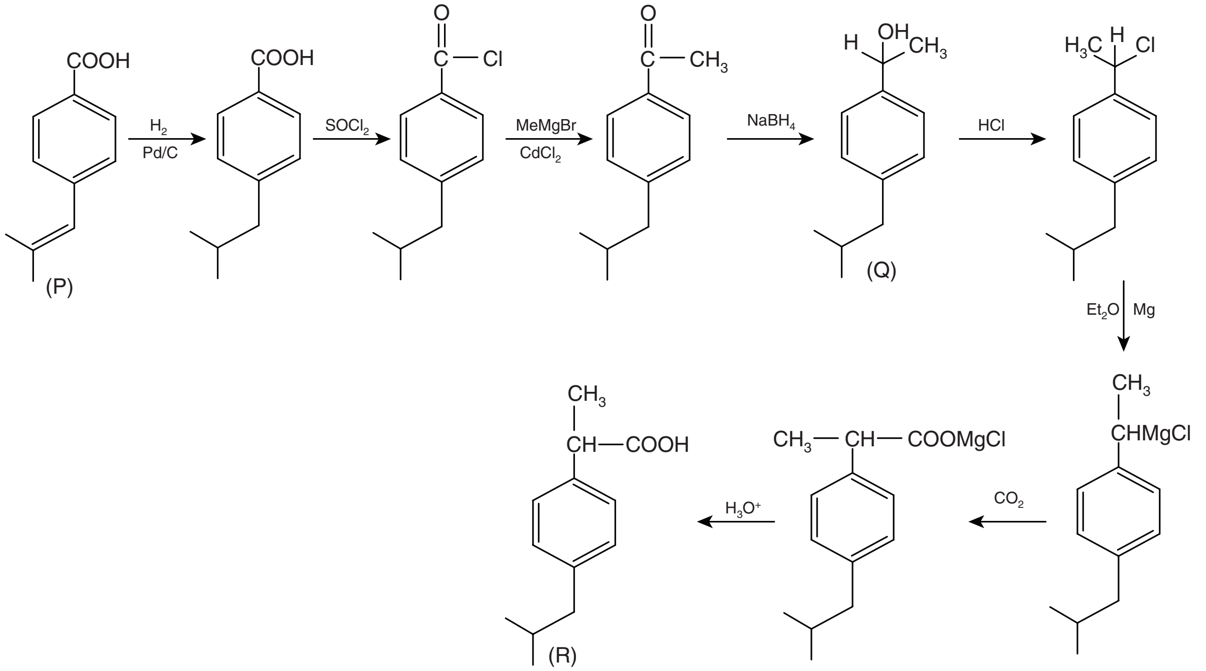


Solution

(A)



PARAGRAPH “A”

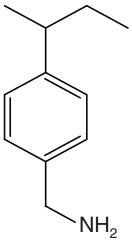
An organic acid **P** ($C_{11}H_{12}O_2$) can easily be oxidized to a dibasic acid which reacts with ethylene glycol to produce a polymer dacron. Upon ozonolysis, **P** gives an aliphatic ketone as one of the products. **P** undergoes the following reaction sequences to furnish **R** *via* **Q**. The compound P also undergoes another set of reactions to produce **S**.

$$\mathbf{S} \xleftarrow[\substack{4.\ CHCl_3,\ KOH,\ \Delta\\ 5.\ H_2/Pd\text{-}C}]{\substack{1.\ H_2/Pd\text{-}C\\ 2.\ NH_3/\Delta\\ 3.\ Br_2/NaOH}} \mathbf{P} \xrightarrow[\substack{3.\ MeMgBr,\ CdCl_2\\ 4.\ NaBH_4}]{\substack{1.\ H_2/Pd\text{-}C\\ 2.\ SOCl_2}} \mathbf{Q} \xrightarrow[\substack{3.\ CO_2\ (dry\ ice)\\ 4.\ H_3O^+}]{\substack{1.\ HCl\\ 2.\ Mg/Et_2O}} \mathbf{R}$$

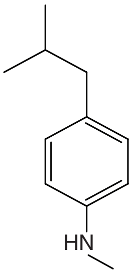
(***There are two questions based on PARAGRAPH “A”, the question given below is one of them***)

18. The compound **S** is

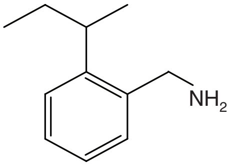
(A)



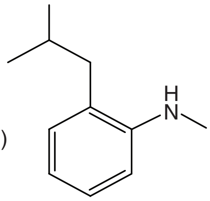
(B)



(C)

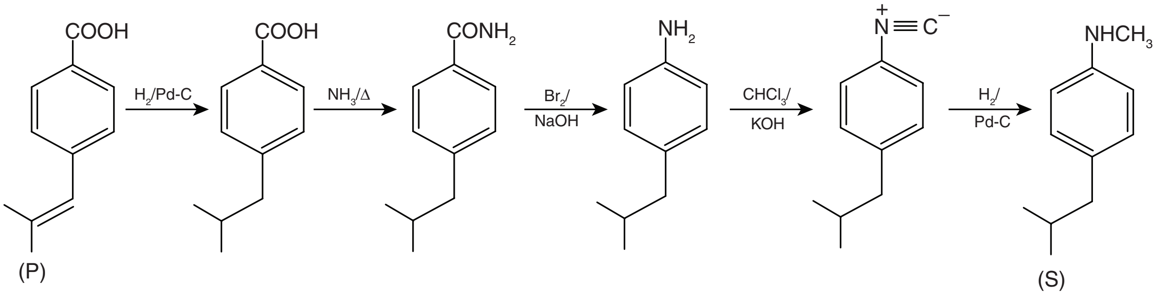


(D)



Solution

(B)


COOH
H2/Pd-C
COOH
NH3/Δ
CONH2
Br2/
NaOH
NH2
CHCl3/
KOH
N≡C
H2/
Pd-C
NHCH3
(P)
(S)

JEE (ADVANCED) 2018
PAPER II (CHEMISTRY)

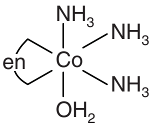
SECTION 1

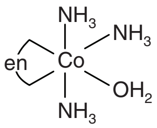
- This section contains **SIX (06)** questions.
- Each question has **FOUR** options for correct answer(s). **ONE OR MORE THAN ONE** of these four option(s) is (are) correct option(s).

1. The correct option(s) regarding the complex $[Co(en)(NH_3)_3(H_2O)]^{3+}$ (en = $H_2NCH_2CH_2NH_2$) is (are)
(A) It has two geometrical isomers.
(B) It will have three geometrical isomers if bidentate 'en' is replaced by two cyanide ligands.
(C) It is paramagnetic.
(D) It absorbs light at longer wavelength as compared to $[Co(en)(NH_3)_4]^{3+}$.

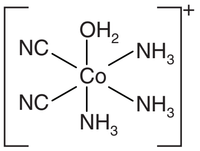
Solution

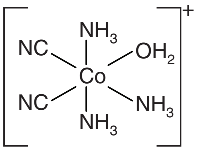
(A) (B) (D) Option (A): Correct. The complex $[Co(en)(NH_3)_3(H_2O)]^{3+}$ has two following isomers:

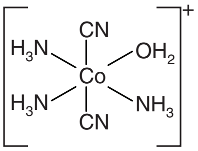




Option (B): Correct. When bidentate 'en' is replaced by two cyanide ligands complex $[Co(CN)_2(NH_3)_3(H_2O)]^+$ will have three following isomers:







Option (C): Incorrect. In complex $[Co(en)(NH_3)_3(H_2O)]^{3+}$, Co is in +3 oxidation, that is, $[Ar]d^6$. In the presence given ligands the complex will have low spin, hence, diamagnetic.
Option (D): Correct. In complex $[Co(en)(NH_3)_4]^{3+}$ there is larger gap between t_{2g} and e_g than in complex $[Co(en)(NH_3)_3(H_2O)]^{3+}$. Hence $[Co(en)(NH_3)_3(H_2O)]^{3+}$ will absorb light at longer wavelength as compared to $[Co(en)(NH_3)_4]^{3+}$.

2. The correct option(s) to distinguish nitrate salts of Mn^{2+} and Cu^{2+} taken separately is (are)
(A) Mn^{2+} shows the characteristic green color in the flame test.
(B) Only Cu^{2+} shows the formation of precipitate by passing H_2S in acidic medium.
(C) Only Mn^{2+} shows the formation of precipitate by passing H_2S in faintly basic medium.
(D) Cu^{2+}/Cu has higher reduction potential than Mn^{2+}/Mn (measured under similar conditions).

Solution

(B) (D) Option (A): Incorrect. Mn^{2+} shows purple color in the flame test.
Option (B): Correct. When H_2S gas is passed through a solution containing Cu^{2+} in the acidic medium, black ppt. is obtained.

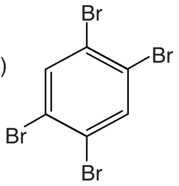
$$Cu^{2+} \xrightarrow[HCl]{H_2S} \underset{\text{(Black ppt.)}}{CuS}$$

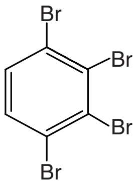
Option (C): Incorrect. Both Mn^{2+} and Cu^{2+}can form precipitate by passing H_2S in faintly basic medium.
Option (D): Correct. Higher reduction potential indicates higher tendency of Cu^{2+} to gain the electrons. Cu^{2+} ion on accepting the electrons gain stability due to fully filled *d*-orbital.

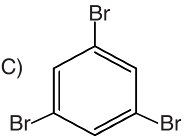
$$\underset{(d^9s^0)}{Cu^{2+}} \rightarrow \underset{(d^{10}s^1)}{Cu} \qquad \underset{(d^5s^0)}{Mn^{2+}} \rightarrow \underset{(d^5s^2)}{Mn}$$

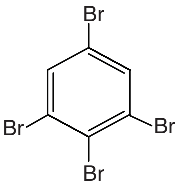
3. Aniline reacts with mixed acid (conc. HNO_3 and conc. H_2SO_4) at 288 K to give **P** (51%), **Q** (47%) and **R** (2%). The major product(s) of the following reaction sequence is (are)

$$R \xrightarrow[\substack{\text{3. } H_3O^+ \\ \text{4. } NaNO_2,\ HCl/273\text{–}278\text{ K} \\ \text{5. EtOH, } \Delta}]{\substack{\text{1. } Ac_2O\text{, Pyridine} \\ \text{2. } Br_2,\ CH_3COOH}} S \xrightarrow[\substack{\text{3. } NaNO_2,\ HCl/273\text{–}278\text{ K} \\ \text{4. } H_3PO_2}]{\substack{\text{1. Sn/HCl} \\ \text{2. } Br_2/H_2O\text{(excess)}}} \text{Major product(s)}$$

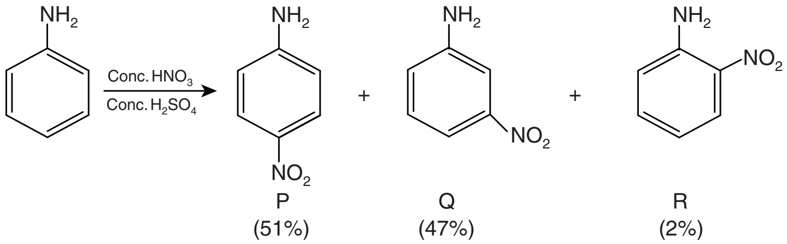
(A)


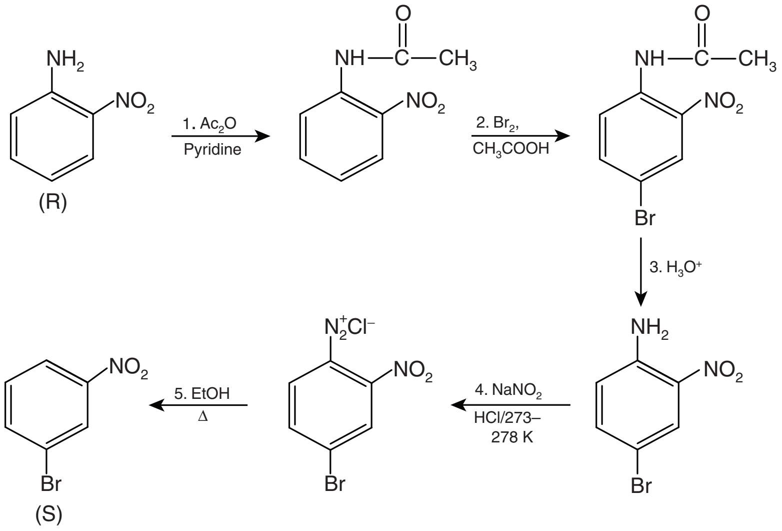
(B)


(C)


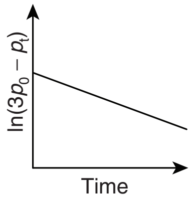
(D)


Solution
(D)

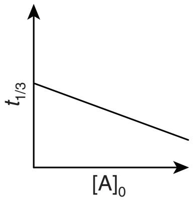




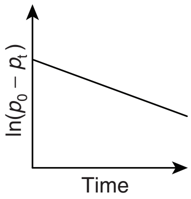
(A)



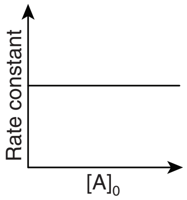
(B)



(C)



(D)



Solution

(A) (D) The reaction can be represented as

$$\begin{array}{lccc} & A(g) & \rightarrow\ 2B(g) & +\ C(g) \\ \text{At } t=0 & p_0 & 0 & 0 \\ \text{At } t=t_{1/3} & p_0-\dfrac{2p_0}{3} & 0 & 0 \\ \text{At } t=t & p_0-x & 2x & x \end{array}$$

Now,
$$p_t = p_0 - x + 2x + x \Rightarrow x = \frac{p_t - p_0}{2}$$

Substituting in the expression $t = \dfrac{1}{k}\ln\left(\dfrac{p_0}{p_0 - x}\right)$, we get

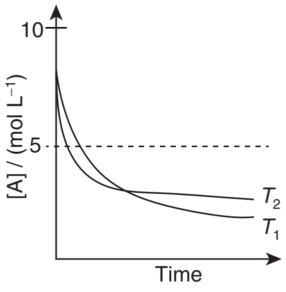
$$t = \frac{1}{k}\ln\left(\frac{p_0}{p_0 - \dfrac{p_t - p_0}{2}}\right) = \frac{1}{k}\ln\left(\frac{2p_0}{3p_0 - p_t}\right)$$

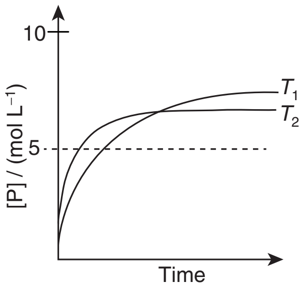
which can be rearranged as

$$\ln(3p_0 - p_t) = -kt + \ln 2p_0$$

Thus, the graph of $\ln(3p_0 - p_t)$ vs t is a straight line having negative slope $-k$ and intercept $\ln 2p_0$ as shown in (A). Also, as rate is independent of initial concentration, so the plot in option (D) is also correct.

6. For a reaction, $A \rightleftharpoons P$, the plots of [A] and [P] with time at temperatures T_1 and T_2 are given below.





If $T_2 > T_1$, the correct statement(s) is (are)
(Assume ΔH^θ and ΔS^θ are independent of temperature and ratio of ln$K$ at T_1 to ln$K$ at T_2 is greater than T_2/T_1 Here H, S, G and K are enthalpy, entropy, Gibbs energy and equilibrium constant, respectively)

(A) $\Delta H^\theta < 0, \Delta S^\theta < 0$
(B) $\Delta G^\theta < 0, \Delta H^\theta > 0$
(C) $\Delta G^\theta < 0, \Delta S^\theta < 0$
(D) $\Delta G^\theta < 0, \Delta S^\theta > 0$

Solution

(A) (C) As we increase the temperature, the concentration of the product reduces. This implies that the reaction is exothermic, and $\Delta H^\theta < 0$.

$$\frac{\ln K_{T_1}}{\ln K_{T_2}} > 1 \Rightarrow \ln K_{T_1} > \ln K_{T_2} \Rightarrow K_{T_1} > K_{T_2}$$

But
$$\frac{\ln K_{T_1}}{\ln K_{T_2}} > \frac{T_2}{T_1}$$

As $\Delta G = -RT \ \text{In}\ K,\ \Delta G^\theta_{T_1} < \Delta G^\theta_{T_2} \Rightarrow \Delta H^\theta_{T_1} - T\,\Delta S^\theta_{T_1} < \Delta H^\theta_{T_2} - T\,\Delta S^\theta_{T_2}$

This is only possible if $\Delta S^\theta < 0$

SECTION 2

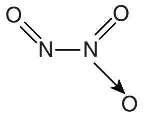
This section contains **EIGHT (08)** questions. The answer to each question is a **NUMERICAL VALUE**.

---

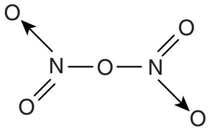
7. The total number of compounds having at least one bridging oxo group among the molecules given below is ______.
N_2O_3, N_2O_5, P_4O_6, P_4O_7, $H_4P_2O_5$, $H_5P_3O_{10}$, $H_2S_2O_3$, $H_2S_2O_5$

Solution

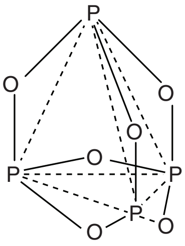
(5)



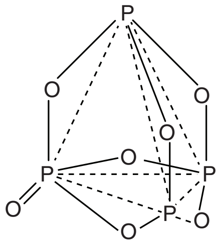
N_2O_3



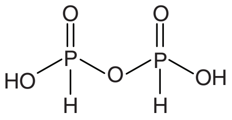
N_2O_5



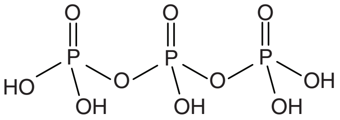
P_4O_6



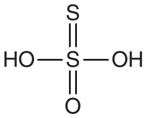
P_4O_7



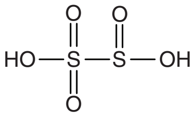
$H_4P_2O_5$



$H_5P_3O_{10}$



$H_2S_2O_3$



$H_2S_2O_5$

8. Galena (an ore) is partially oxidized by passing air through it at high temperature. After some time, the passage of air is stopped, but the heating is continued in a closed furnace such that the contents undergo self-reduction. The weight (in kg) of Pb produced per kg of O_2 consumed is _______.
(Atomic weights in g mol^{-1}: O = 16, S = 32, Pb = 207)

Solution

(6.47) The steps involved in the oxidation of galena (PbS) are as follows:

$$2\text{PbS}+3\text{O}_2 \rightarrow 2\text{PbO}+2\text{SO}_2$$
$$2\text{PbO}+\text{PbS} \rightarrow 3\text{Pb}+\text{SO}_2$$

As per the above reactions, we can conclude that
3 mol of O_2 produces 3 mol of lead
96 kg of O_2 produces 621 kg of lead

Therefore, 1 kg of O_2 will produce $\frac{621}{96}\times 1 = 6.47\,\text{kg}$ of Pb.

9. To measure the quantity of $MnCl_2$ dissolved in an aqueous solution, it was completely converted to $KMnO_4$ using the reaction,
$MnCl_2 + K_2S_2O_8 + H_2O \rightarrow KMnO_4 + H_2SO_4 + HCl$ (equation not balanced).
Few drops of concentrated HCl were added to this solution and gently warmed. Further, oxalic acid (225 mg) was added in portions till the color of the permanganate ion disappeared. The quantity of $MnCl_2$ (in mg) present in the initial solution is _______.
(Atomic weights in g mol^{-1}: Mn = 55, Cl = 35.5)

Solution

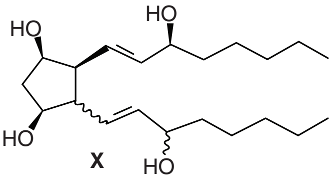
(126) The balanced equation can be written as

$$2\text{MnCl}_2 + 5\text{K}_2\text{S}_2\text{O}_8 + 8\text{H}_2\text{O} \rightarrow 2\text{KMnO}_4 + 4\text{K}_2\text{SO}_4 + 6\text{H}_2\text{SO}_4 + 4\text{HCl}$$
$$2\text{KMnO}_4 + 5\text{H}_2\text{C}_2\text{O}_4 + 3\text{H}_2\text{SO}_4 \rightarrow \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 8\text{H}_2\text{O} + 10\text{CO}_2$$

$$\text{Millimoles of KMnO}_4 = \text{Millimoles of H}_2\text{C}_2\text{O}_4$$
$$\text{Millimole MnCl}_2 \times 5 = \left(\frac{225}{90}\right)\times 2$$

So, millimole of $MnCl_2$ = 1 = 126 mg.

10. For the given compound **X**, the total number of optically active stereoisomers is _______.



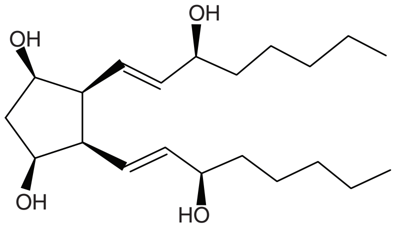
X

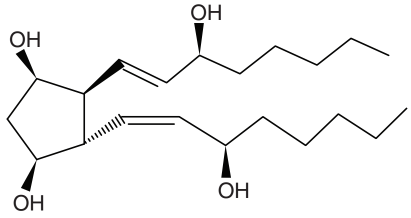
◀ This type of bond indicates that the configuration at the specific carbon and the geometry of the double bond is fixed.

〰 This type of bond indicates that the configuration at the specific carbon and the geometry of the double bond is not fixed.

Solution

(7) There are total 7 optically active stereoisomers. Their structures are as follows:


(optically inactive)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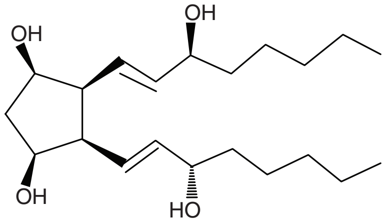
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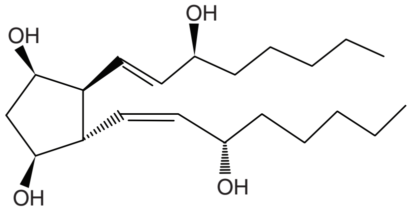
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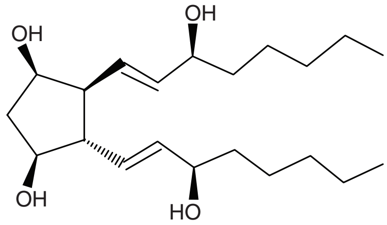
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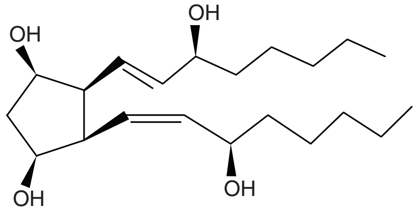
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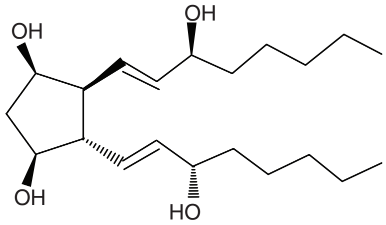
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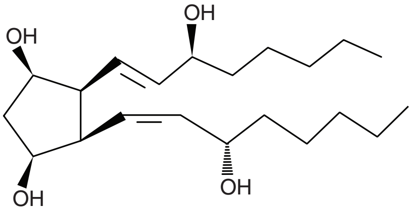
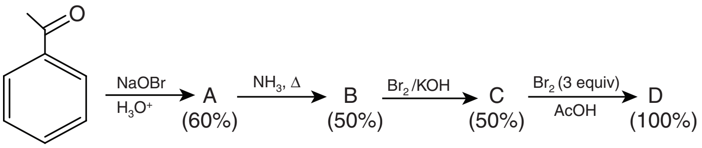
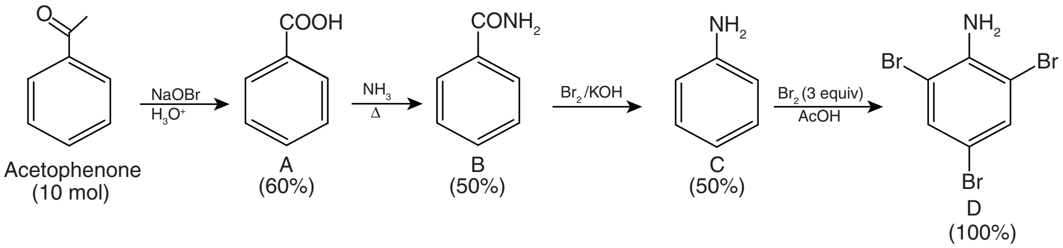

(optically active)

11. In the following reaction sequence, the amount of **D** (in g) formed from 10 mol of acetophenone is _______. (Atomic weights in g mol^{-1}: H = 1, C = 12, N = 14, O = 16, Br = 80. The yield (%) corresponding to the product in each step is given in the parenthesis)



Solution

(495)



The amount of D formed in mol is $\frac{60}{100}\times\frac{50}{100}\times\frac{50}{100}\times 10 = 1.5\,\text{mol}$

Amount of D in grams is = 1.5 × 330 g = 495 g

12. The surface of copper gets tarnished by the formation of copper oxide. N_2 gas was passed to prevent the oxide formation during heating of copper at 1250 K. However, the N_2 gas contains 1 mole % of water vapor as impurity. The water vapor oxidizes copper as per the reaction given below:

$$2Cu(s) + H_2O(g) \rightarrow Cu_2O(s) + H_2(g)$$

p_{H_2} is the minimum partial pressure of H_2 (in bar) needed to prevent the oxidation at 1250 K. The value of $\ln(p_{H_2})$ is ________.

(Given: total pressure = 1 bar, R (universal gas constant) = 8 J K^{-1} mol^{-1}, ln(10) = 2.3. Cu(s) and $Cu_2O(s)$ are mutually immiscible.

At 1250 K: $2Cu(s) + \frac{1}{2}O_2(g) \rightarrow Cu_2O(s);\ \Delta G^\circ = -78{,}000\ \text{J mol}^{-1}$

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g);\ \ \Delta G^\circ = -1{,}78{,}000\ \text{J mol}^{-1}$; G is the Gibbs energy)

Solution

(–14.6)

$$2Cu(s)+\frac{1}{2}O_2(g) \rightarrow Cu_2O(s); \quad \Delta G^\circ = -78{,}000\ \text{J mol}^{-1} \tag{1}$$

$$H_2(g)+\frac{1}{2}O_2(g) \rightarrow H_2O(g); \quad \Delta G^\circ = -1{,}78{,}000\ \text{J mol}^{-1} \tag{2}$$

Subtracting Eq. (1) – Eq. (2), we get

$$2Cu(s)+H_2O(g) \rightarrow Cu_2O(s)+H_2(g); \quad \Delta G^\circ = +100000\ \text{J mol}^{-1} \tag{3}$$

Now,
$$\Delta G = \Delta G^\circ + RT\ln\left(\frac{p_{H_2}}{p_{H_2O}}\right)$$

For the reaction (3) to not occur,

$$\Delta G > 0 \text{ or } \Delta G^\circ + RT\ln\left(\frac{p_{H_2}}{p_{H_2O}}\right) > 0$$

$$\Rightarrow 100000 + 8\times 1250\ln\left(\frac{p_{H_2}}{p_{H_2O}}\right) > 0$$

$$\Rightarrow 100000 + 8\times 1250\ln\left(\frac{p_{H_2}}{p_{H_2O}}\right) > \frac{-100000}{8\times 1250}$$

$$\Rightarrow \ln\left(\frac{p_{H_2}}{p_{H_2O}}\right) > -10$$

$$\ln p_{H_2} > -10 + \ln p_{H_2O}$$

Now, $p_{\mathrm{H_2O}} = x_{\mathrm{H_2O}} \times p_{\mathrm{T}} = 0.01 \times 1 = 10^{-2}$

So, $\ln p_{\mathrm{H_2}} > -10 - 2\ln 10 \Rightarrow p_{\mathrm{H_2}} > -14.6$ bar

13. Consider the following reversible reaction,

$$\mathrm{A(g) + B(g) \rightleftharpoons AB(g)}.$$

The activation energy of the backward reaction exceeds that of the forward reaction by $2RT$ (in J mol^{-1}). If the pre-exponential factor of the forward reaction is 4 times that of the reverse reaction, the absolute value of ΔG^θ (in J mol^{-1}) for the reaction at 300 K is _______.
(Given; ln(2) = 0.7, $RT = 2500$ J mol^{-1} at 300 K and G is the Gibbs energy)

Solution

(–8466 J mol^{-1})

$$\Delta G^\theta = -RT \ln K$$

where

$$K = \frac{K_{\mathrm{f}}}{K_{\mathrm{b}}} = \frac{A_{\mathrm{f}} e^{-E_{\mathrm{a_f}}/RT}}{A_{\mathrm{b}} e^{-E_{\mathrm{a_b}}/RT}}$$

Now, given that $A_{\mathrm{f}} = 4A_{\mathrm{b}}$ and $E_{\mathrm{a_b}} - E_{\mathrm{a_f}} = 2RT$. Substituting, we get

$$K = \frac{K_{\mathrm{f}}}{K_{\mathrm{b}}} = 4e^{(E_{\mathrm{a_b}} - E_{\mathrm{a_f}})/RT} = 4e^2$$

Therefore, $\Delta G^\theta = -RT \ln(4e^2) = -2500 \times [\ln(4) + 2] = -8466 \text{ J mol}^{-1}$

14. Consider an electrochemical cell: A(s) | A^{n+} (aq, 2 M) || B^{2n+} (aq, 1 M) | B(s). The value of ΔH^θ for the cell reaction is twice that of ΔG^θ at 300 K. If the emf of the cell is zero, the ΔS^θ (in J K^{-1} mol^{-1}) of the cell reaction per mole of B formed at 300 K is _______.
(Given: ln(2) = 0.7, R (universal gas constant) = 8.3 J K^{-1} mol^{-1}. H, S and G are enthalpy, entropy and Gibbs energy, respectively)

Solution

(–11.62 JK^{-1}mol^{-1}) The half-cell reactions are

$$\mathrm{A(s) \longrightarrow A^{n+}(aq) + }ne^- \quad (1)$$

$$\mathrm{B^{2n+}(aq) + 2}ne^- \mathrm{\longrightarrow B(s)} \quad (2)$$

Adding Eq. (1) and Eq. (2), we get

$$\mathrm{2A(s) + B^{2n+}(aq) \longrightarrow 2A^{n+}(aq) + B(s)}$$

Given that $\Delta H^\theta = 2\Delta G^\theta$ and $E_{\text{cell}} = 0$, so

$$\Delta G^\theta = \Delta H^\theta - T\Delta S^\theta \Rightarrow \Delta S^\theta = \frac{\Delta G^\theta}{T} = \frac{-RT \ln K}{T}$$

$$\Rightarrow \Delta S^\theta = -R \ln \frac{[\mathrm{A}^{n+}]^2}{[\mathrm{B}^{2n+}]} = -8.3 \times \ln 4 = -11.5 \text{ J K}^{-1} \text{ mol}^{-1}$$

SECTION 3

- This section contains **FOUR (04)** questions.
- Each question has **TWO (02)** matching lists: **LIST-I** and **LIST-II**.
- FOUR options are given representing matching of elements from **LIST-I** and **LIST-II. ONLY ONE** of these four options corresponds to a correct matching.

15. Match each set of hybrid orbitals from LIST-I with complex(es) given in LIST-II.

LIST-I	LIST-II
P. dsp^2	**1.** $[FeF_6]^{4-}$
Q. sp^3	**2.** $[Ti(H_2O)_3Cl_3]$
R. sp^3d^2	**3.** $[Cr(NH_3)_6]^{3+}$
S. d^2sp^3	**4.** $[FeCl_4]^{2-}$
	5. $[Ni(CO)]_4$
	6. $[Ni(CN)_4]^{2-}$

The correct option is

(A) P → 5; Q → 4, 6; R → 2, 3; S → 1

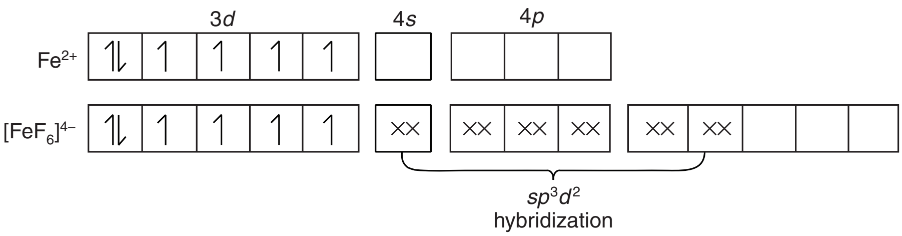
(B) P → 5, 6; Q → 4; R → 3; S → 1, 2

(C) P → 6; Q → 4, 5; R → 1; S → 2, 3

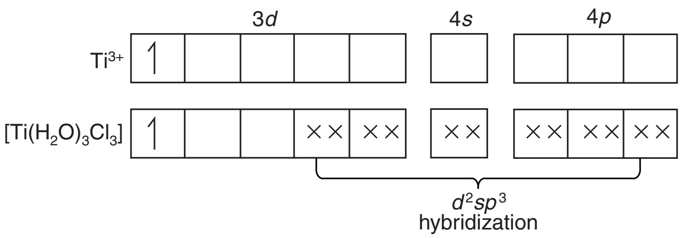
(D) P → 4, 6; Q → 5, 6; R → 1, 2; S → 3

Solution

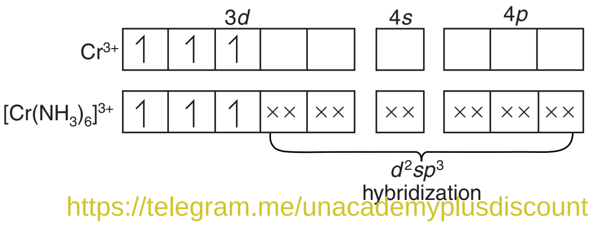
(C) $[FeF_6]^{4-}$: The arrangement of electrons in Fe^{2+} ($3d^6$) will be



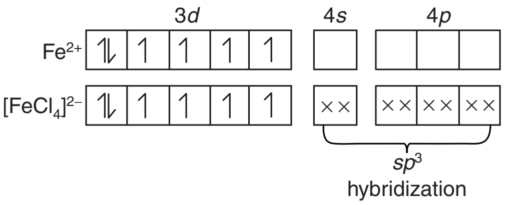
$[Ti(H_2O)_3Cl_3]$: The arrangement of electrons in Ti^{3+} ($3d^1$) will be



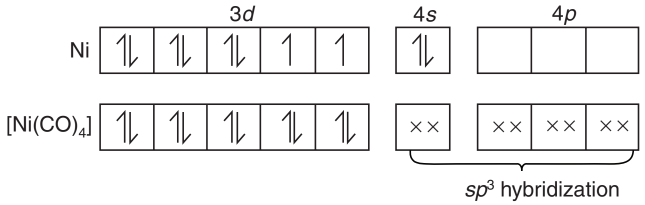
$[Cr(NH_3)_6]^{3+}$: The arrangement of electrons in Cr^{3+} ($3d^3$) will be



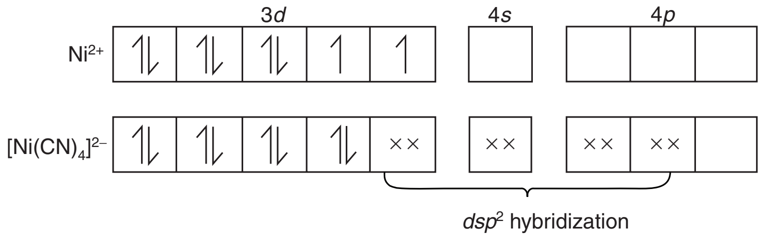
$[FeCl_4]^{2-}$: The arrangement of electrons in Fe^{2+} ($3d^6$) will be



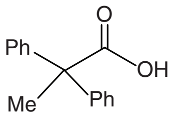
$[Ni(CO)_4]$: The arrangement of electrons in Ni^0 ($3d^8 4s^2$) will be



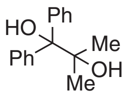
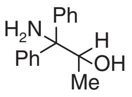
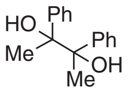
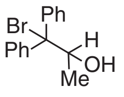
$[Ni(CN)_4]^{2-}$: The arrangement of electrons in Ni^{2+} ($3d^8$) will be



16. The desired product **X** can be prepared by reacting the major product of the reactions in LIST-I with one or more appropriate reagents in LIST-II.
(Given, order of migratory aptitude: aryl > alkyl > hydrogen)



X

LIST-I	LIST-II
P.  + H_2SO_4	**1.** I_2, NaOH
Q.  + HNO_2	**2.** $[Ag(NH_3)_2]OH$
R.  + H_2SO_4	**3.** Fehling solution
S.  + $AgNO_3$	**4.** HCHO, NaOH
	5. NaOBr

The correct option is

(A) P → 1; Q → 2, 3; R → 1, 4; S → 2, 4

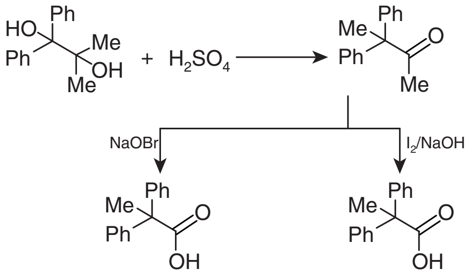
(B) P → 1, 5; Q → 3, 4; R → 4, 5; S → 3

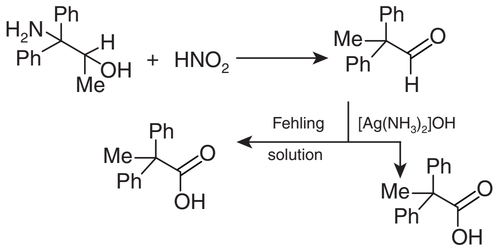
(C) P → 1, 5; Q → 3, 4; R → 5; S → 2, 4

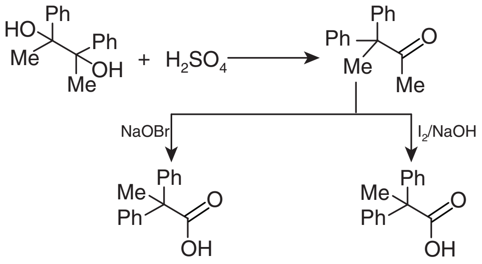
(D) P → 1, 5; Q → 2, 3; R → 1, 5; S → 2, 3

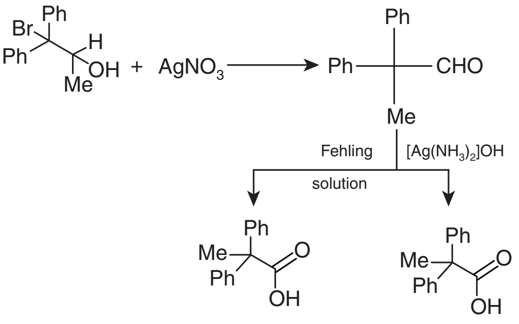
Solution

(D) The reactions are as follows:

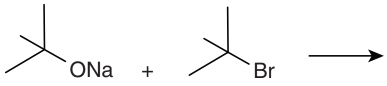
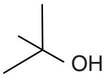
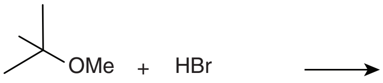
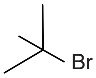
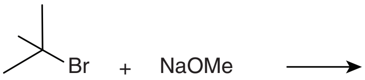
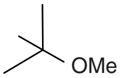
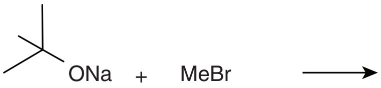
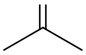
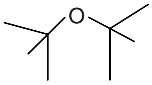








17. LIST-I contains reactions and LIST-II contains major products.

LIST-I	LIST-II
P. 	**1.** 
Q. 	**2.** 
R. 	**3.** 
S. 	**4.** 
	5. 

Match each reaction in LIST-I with one or more products in LIST-II and choose the correct option.

(A) P → 1, 5; Q → 2; R → 3; S → 4

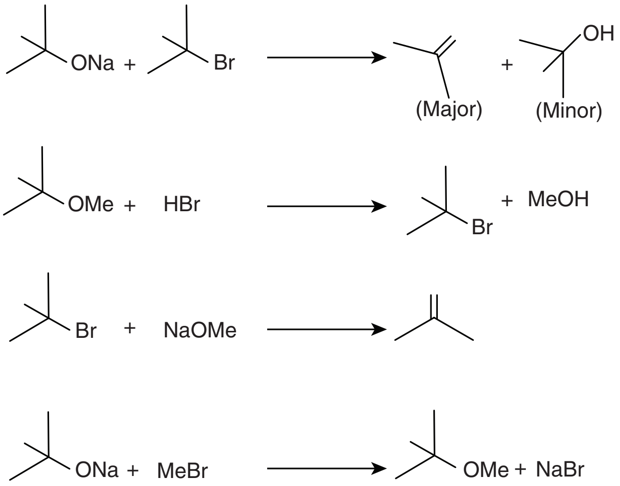
(B) P → 1, 4; Q → 2; R → 4; S → 3

(C) P → 1, 4; Q → 1, 2; R → 3, 4; S → 4

(D) P → 4, 5; Q → 4; R → 4; S → 3, 4

Solution

(B) With *tertiary* halides, steric hindrance in the substrate is severe, thus, elimination is highly favored, especially when the reaction is carried out at higher temperatures.



18. Dilution processes of different aqueous solutions, with water, are given in LIST-I. The effects of dilution of the solutions on [H^+] are given in

(**Note:** Degree of dissociation (α) of weak acid and weak base is << 1; degree of hydrolysis of salt << 1; [H^+] represents the concentration of H^+ ions)

LIST-I	LIST-II
P. (10 mL of 0.1 M NaOH + 20 mL of 0.1 M acetic acid) diluted to 60 mL	**1.** the value of $[H^+]$ does not change on dilution
Q. (20 mL of 0.1 M NaOH + 20 mL of 0.1 M acetic acid) diluted to 80 mL	**2.** the value of $[H^+]$ changes to half of its initial value on dilution
R. (20 mL of 0.1 M HCl + 20 mL of 0.1 M ammonia solution) diluted to 80 mL	**3.** the value of $[H^+]$ changes to two times of its initial value on dilution
S. 10 mL saturated solution of $Ni(OH)_2$ in equilibrium with excess solid $Ni(OH)_2$ is diluted to 20 mL (solid $Ni(OH)_2$ is still present after dilution).	**4.** the value of $[H^+]$ changes to $\frac{1}{\sqrt{2}}$ times of its initial value on dilution
	5. the value of $[H^+]$ changes to $\sqrt{2}$ times of its initial value on dilution

Match each process given in LIST-I with one or more effect(s) in LIST-II. The correct option is

(A) P → 4; Q → 2; R → 3; S → 1
(B) P → 4; Q → 3; R → 2; S → 3
(C) P → 1; Q → 4; R → 5; S → 3
(D) P → 1; Q → 5; R → 4; S → 1

Solution

(D)

$$\begin{array}{ccccc} NaOH & + & CH_3COOH & \rightarrow & CH_3COONa + H_2O \\ 10 \times 0.1 = 1\ \text{mmol} & & 20 \times 0.1 = 2\ \text{mmol} & & \end{array}$$

$$\left[CH_3COO^-\right] = \frac{20 \times 0.1 - 10 \times 0.1}{30} = \frac{1}{30}$$

Since it is a buffer solution, with 1 mmol of CH_3COOH and 1 mmol of CH_3COONa in solution. So, (P) → (1).

$$\begin{array}{ccccc} NaOH & + & CH_3COOH & \rightarrow & CH_3COONa + H_2O \\ 20 \times 0.1 = 2\ \text{mmol} & & 20 \times 0.1 = 2\ \text{mmol} & & \end{array}$$

Since the solution contains 2 mmol of CH_3COONa in 40 ml solution. So, for a salt of weak acid and strong base, we have

$$[H^+]_{\text{initial}} = \sqrt{\frac{K_w K_a}{C}}$$

On dilution to 80 ml, C becomes $C/2$, so $[H^+]_{\text{new}} = \sqrt{\frac{K_w K_a}{C/2}} = [H^+]_{\text{initial}} \times \sqrt{2}$. So, (Q) → (5)

$$\begin{array}{ccccc} HCl & + & NH_3 & \rightarrow & NH_4Cl \\ 20 \times 0.1 = 2\ \text{mmol} & & 20 \times 0.1 = 2\ \text{mmol} & & \end{array}$$

Since the solution contains 2 mmol of CH_3COONa in 40 mL solution. So, for a salt of strong acid and weak base, we have

$$[H^+]_{\text{initial}} = \sqrt{\frac{K_w C}{K_b}}$$

On dilution to 80 mL, C becomes $C/2$, so $[H^+]_{\text{new}} = \sqrt{\frac{K_w C}{2K_b}} = [H^+]_{\text{initial}} / \sqrt{2}$. So, (R) → (4)

$$Ni(OH)_2(s) \rightarrow Ni^{2+}(aq) + 2OH^-(aq)$$

As it is a sparingly soluble salt, there is no change in $[OH^-]$ on dilution. So, (S) → (1)

JEE Main 2019 (January 9, Shift 1)

CHEMISTRY

1. Two complexes $[Cr(H_2O)_6]Cl_3$ (A) and $[Cr(NH_3)_6]Cl_3$ (B) are violet and yellow coloured, respectively. The incorrect statement regarding them is:

(1) Δ_o values of (A) and (B) are calculated from the energies of violet and yellow light, respectively.

(2) both are paramagnetic with three unpaired electrons.

(3) both absorb energies corresponding to their complementary colors.

(4) Δ_o values for (A) is less than that of (B).

2. The correct decreasing order for acid strength is:

(1) $NO_2CH_2COOH > FCH_2COOH > CNCH_2COOH > ClCH_2COOH$

(2) $FCH_2COOH > NCCH_2COOH > NO_2CH_2COOH > ClCH_2COOH$

(3) $CNCH_2COOH > O_2NCH_2COOH > FCH_2COOH > ClCH_2COOH$

(4) $NO_2CH_2COOH > NCCH_2COOH > FCH_2COOH > ClCH_2COOH$

3. The major product of following reaction is:

$$R-C\equiv N \xrightarrow[\text{(ii) } H_2O]{\text{(i) AlH}(i-\text{Bu})_2} ?$$

(1) RCOOH (2) $RCONH_2$

(3) RCHO (4) RCH_2NH_2

4. The highest value of the calculated spin-only magnetic moment (in BM) among all the transition metal complexes is:

(1) 5.92 (2) 6.93

(3) 3.87 (4) 4.90

5. 0.5 moles of gas A and x moles of gas B exert a pressure of 200 Pa in a container of volume 10 m^3 at 1000 K. Given R is the gas constant in $JK^{-1}\ mol^{-1}$, x is:

(1) $\dfrac{2R}{4+R}$ (2) $\dfrac{2R}{4-R}$

(3) $\dfrac{4+R}{2R}$ (4) $\dfrac{4-R}{2R}$

6. The one that is extensively used as a piezoelectric material is:

(1) tridymite (2) amorphous silica

(3) quartz (4) mica

7. Correct statements among a to d regarding silicones are:

(a) They are polymers with hydrophobic character.

(b) They are biocompatible.

(c) In general, they have high thermal stability and low dielectric strength.

(d) Usually, they are resistant to oxidation and used as greases.

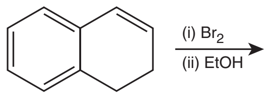
(1) (a), (b), (c) and (d)

(2) (a), (b) and (c) only

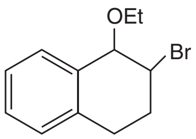
(3) (a) and (b) only

(4) (a), (b) and (d) only

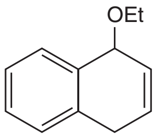
8. The major product of the following reaction is:



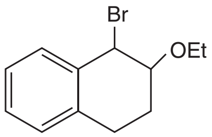
(1)



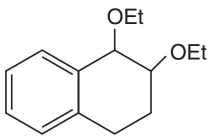
(2)



(3)



(4)



9. In general, the properties that decrease and increase down a group in the periodic table, respectively, are:

(1) atomic radius and electronegativity.

(2) electron gain enthalpy and electronegativity.

(3) electronegativity and atomic radius.

(4) electronegativity and electron gain enthalpy.

10. A solution of sodium sulfate contains 92 g of Na^+ ions per kilogram of water. The molality of Na^+ ions in that solution in mol kg^{-1} is:

(1) 12 (2) 4

(3) 8 (4) 16

11. The correct match between Item-I and Item-II is:

Item-I (drug)	**Item-II** (test)
(A)Chloroxylenol	(P) Carbylamine test
(B) Norethindron	(Q) Sodium hydrogen-carbonate test
(C) Sulphapyridine	(R) Ferric chloride test
(D) Penicillin	(S) Baeyer's test

(1) A → R; B → P; C → S; D → Q

(2) A → Q; B → S; C → P; D → R

(3) A → R; B → S; C → P; D → Q

(4) A → Q; B → P; C → S; D → R

12. A water sample has ppm level concentration of the following metals: Fe = 0.2; Mn = 5.0, Cu = 3.0; Zn = 5.0. The metal that makes the water sample unsuitable for drinking is:

(1) Cu (2) Mn

(3) Fe (4) Zn

13. The anodic half-cell of lead-acid battery is recharged using electricity of 0.05 Faraday. The amount of $PbSO_4$ electrolyzed in g during the process is : (Molar mass of $PbSO_4$ = 303 g mol^{-1})

(1) 22.8 (2) 15.2

(3) 7.6 (4) 11.4

14. Which one of the following statements regarding Henry's law is not correct?

(1) Higher the value of K_H at a given pressure, higher is the solubility of the gas in the liquids.

(2) Different gases have different K_H (Henry's law constant) values at the same temperature.

(3) The partial pressure of the gas in vapour phase is proportional to the mole fraction of the gas in the solution.

(4) The value of K_H increases with increase of temperature and K_H is function of the nature of the gas

15. The following results were obtained during kinetic studies of the reaction;

$$2A + B \rightarrow \text{Products}$$

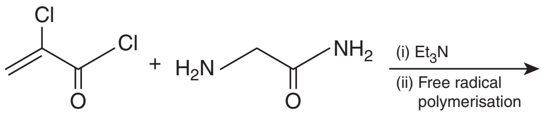
Experiment	**[A] (in mol L^{-1})**	**[B] (in mol L^{-1})**	**Initial Rate of Reaction (in mol L^{-1} min^{-1})**
I	0.10	0.20	6.93×10^{-3}
II	0.10	0.25	6.93×10^{-3}
III	0.20	0.30	1.386×10^{-2}

The time (in minutes) required to consume half of A is:

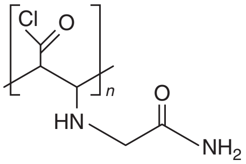
(1) 5 (2) 10

(3) 1 (4) 100

16. Major product of the following reaction is:



(1)



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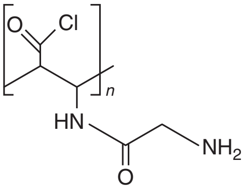

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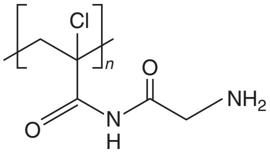

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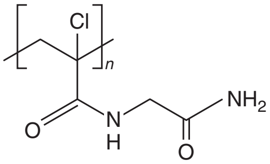


17. The alkaline earth metal nitrate that does not crystallise with water molecules, is:

(1) $Mg(NO_3)_2$ (2) $Sr(NO_3)_2$

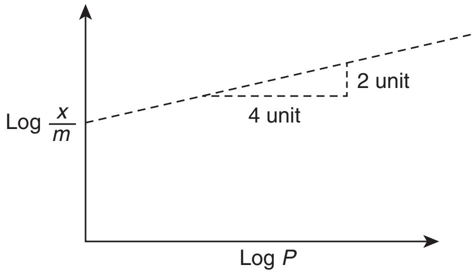
(3) $Ca(NO_3)_2$ (4) $Ba(NO_3)_2$

18. 20 mL of 0.1 M H_2SO_4 solution is added to 30 mL of 0.2 M NH_4OH solution. The pH of the resultant mixture is : [pK_b of $NH_4OH = 4.7$].

(1) 5.2 (2) 9.0

(3) 5.0 (4) 9.4

19. Adsorption of a gas follows Freundlich adsorption isotherm. In the given plot, x is the mass of the gas adsorbed on mass m of the adsorbent at pressure p. $\frac{x}{m}$ is proportional to:



(1) p^2 (2) $p^{1/4}$

(3) $p^{1/2}$ (4) p

20. Which amongst the following is the strongest acid?

(1) $CHBr_3$ (2) CHI_3

(3) $CH(CN)_3$ (4) $CHCl_3$

21. The ore that contains both iron and copper is:

(1) copper pyrites (2) malachite

(3) dolomite (4) azurite

22. For emission line of atomic hydrogen from $n_i = 8$ to $n_f = n$, the plot of wave number $(\bar{v})$ against $\left(\frac{1}{n^2}\right)$ will be (The Rydberg constant, R_H is in wave number unit)

(1) Linear with intercept $-R_H$

(2) Non linear

(3) Linear with slope R_H

(4) Linear with slope $-R_H$

23. The isotopes of hydrogen are:

(1) Tritium and protium only

(2) Protium and deuterium only

(3) Protium, deuterium and tritium

(4) Deuterium and tritium only

24. According to molecular orbital theory, which of the following is true with respect to Li_2^+ and Li_2^-?

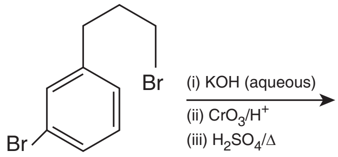
(1) Li_2^+ is unstable and Li_2^- is stable

(2) Li_2^+ is stable and Li_2^- is unstable

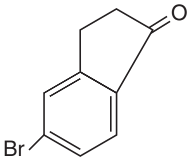
(3) Both are stable

(4) Both are unstable

25. The major product of the following reaction is:



(1)



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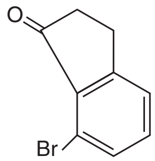

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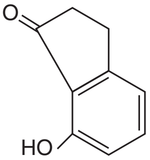

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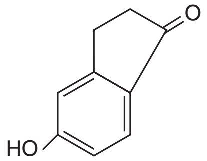


26. Aluminium is usually found in +3 oxidation state. In contrast, thallium exists in +1 and +3 oxidation states. This is due to:

(1) inert pair effect

(2) diagonal relationship

(3) lattice effect

(4) lanthanoid contraction

27. The increasing order of pK_a of the following amino acids in aqueous solution is:

Gly Asp Lys Arg

(1) Asp < Gly < Arg < Lys

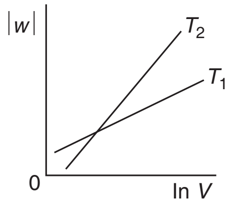
(2) Gly < Asp < Arg < Lys

(3) Asp < Gly < Lys < Arg

(4) Arg < Lys < Gly < Asp

28. Consider the reversible isothermal expansion of an ideal gas in a closed system at two different temperatures T_1 and T_2 ($T_1 < T_2$). The correct graphical depiction of the dependence of work done (w) on the final volume (V) is:

(1)



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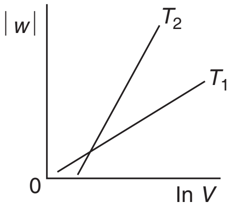

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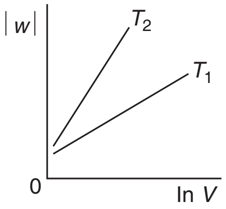

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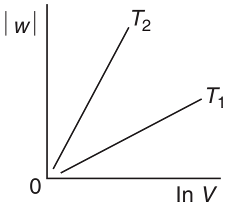
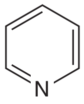
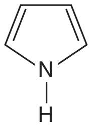


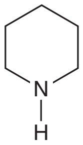
29. Arrange the following amines in the decreasing order of basicity:



I



II



III

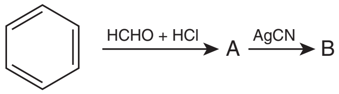
(1) I > II > III

(2) III > I > II

(3) III > II > I

(4) I > III > II

30. The compounds A and B in the following reaction are, respectively:



(1) A = Benzyl alcohol, B = Benzyl cyanide

(2) A = Benzyl chloride, B = Benzyl cyanide

(3) A = Benzyl alcohol, B = Benzyl isocyanide

(4) A = Benzyl chloride, B = Benzyl isocyanide

JEE Main 2019 (January 9, Shift 2)

CHEMISTRY

1. The entropy change associated with the conversion of 1 kg of ice at 273 K to water vapours at 383 K is:

(Specific heat of water liquid and water vapour are 4.2 kJ K^{-1} kg^{-1} and 2.0 kJ K^{-1} kg^{-1}; heat of liquid fusion and vapourisation of water are 334 kJ kg^{-1} and 2491 kJ kg^{-1}, respectively). (log 273 = 2.436, log 373 = 2.572, log 383 = 2.583)

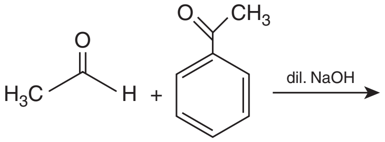
(1) 7.90 kJ kg^{-1} K^{-1}
(2) 2.64 kJ kg^{-1} K^{-1}
(3) 8.49 kJ kg^{-1} K^{-1}
(4) 9.26 kJ kg^{-1} K^{-1}

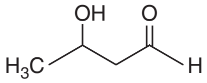
2. For the following reaction, the mass of water produced from 445 g of $C_{57}H_{110}O_6$ is:

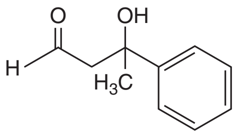
$$2C_{57}H_{110}O_6(s) + 163\ O_2(g) \rightarrow 114\ CO_2(g) + 110\ H_2O(l)$$

(1) 490 g
(2) 445 g
(3) 495 g
(4) 890 g

3. The major product formed in the following reaction is:



(1)


(2)


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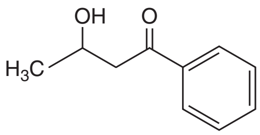

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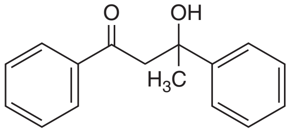
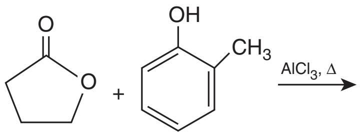
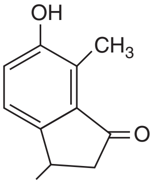


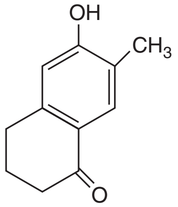
4. Which of the following conditions in drinking water causes methemoglobinemia?

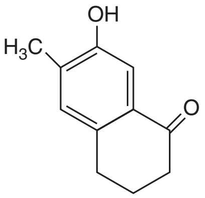
(1) >50 ppm of lead
(2) >50 ppm of chloride
(3) >50 ppm of nitrate
(4) >100 ppm of sulphate

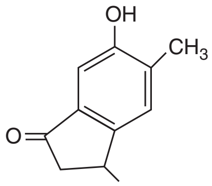
5. The major product of the following reaction is:



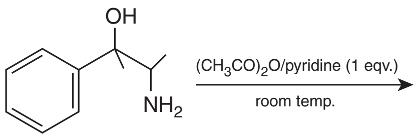
(1)


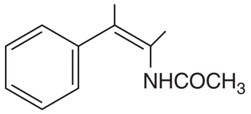
(2)


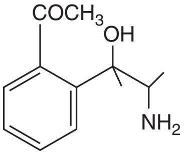
(3)


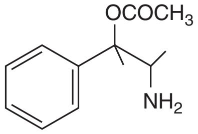
(4)


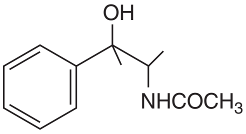
6. The major product obtained in the following reaction is:



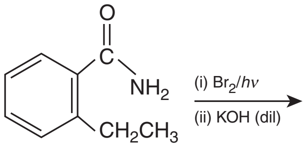
(1) 

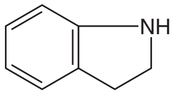
(2) 

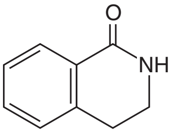
(3) 

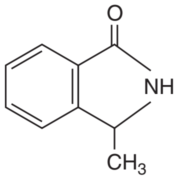
(4) 

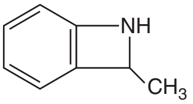
7. The major product of the following reaction is:



(1) 

(2) 

(3) 

(4) 

8. The correct match between Item I and Item II is:

Item I	**Item II**
(A) Benzaldehyde	(P) Mobile phase
(B) Alumina	(Q) Adsorbent
(C) Acetonitrile	(R) Adsorbate

(1) (A) → (Q); (B) → (P); (C) → (R)

(2) (A) → (R); (B) → (Q); (C) → (P)

(3) (A) → (Q); (B) → (R); (C) → (P)

(4) (A) → (P); (B) → (R); (C) → (Q)

9. The metal that forms nitride by reacting directly with N_2 of air, is:

(1) K (2) Li

(3) Rb (4) Cs

10. For coagulation of arsenious sulphide sol, which one of the following salt solution will be most effective?

(1) $BaCl_2$ (2) $AlCl_3$

(3) NaCl (4) Na_3PO_4

11. The complex that has highest crystal field splitting energy (Δ), is:

(1) $[Co(NH_3)_5(H_2O)]Cl_3$ (2) $K_2[CoCl_4]$

(3) $[Co(NH_3)_5Cl]Cl_2$ (4) $K_3[Co(CN)_6]$

12. The pH of rain water, is approximately:

(1) 5.6 (2) 7.5

(3) 7.0 (4) 6.5

13. Consider the following reversible chemical reactions:

$$A_2(g) + B_2(g) \xrightleftharpoons{K_1} 2AB(g) \quad ...(1)$$

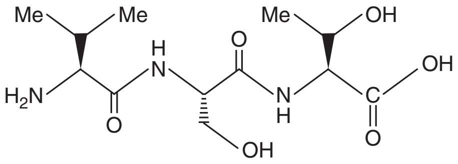
$$6AB(g) \xrightleftharpoons{K_2} 3A_2(g) + 3B_2(g) \quad ...(2)$$

The relation between K_1 and K_2 is:

(1) $K_1K_2 = \frac{1}{3}$ (2) $K_2 = K_1^3$

(3) $K_2 = K_1^{-3}$ (4) $K_1K_2 = 3$

14. The correct sequence of amino acids present in the tripeptide given below is:



(1) Val – Ser – Thr (2) Thr – Ser – Val

(3) Leu – Ser – Thr (4) Thr – Ser – Leu

15. For the reaction, 2A + B → products, when the concentrations of A and B both were doubled, the rate of the reaction increased from 0.3 mol L^{-1} s^{-1} to 2.4 mol L^{-1} s^{-1}. When the concentration of A alone is doubled, the rate increased from 0.3 mol L^{-1} s^{-1} to 0.6 mol L^{-1} s^{-1}.

Which one of the following statements is correct?

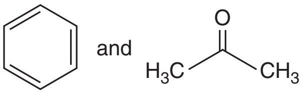
(1) Total order of the reaction is 4

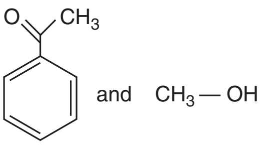
(2) Order of the reaction with respect to B is 2

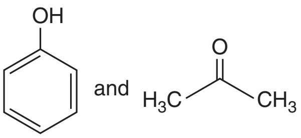
(3) Order of the reaction with respect to B is 1

(4) Order of the reaction with respect to A is 2

16. The products formed in the reaction of cumene with O_2 followed by treatment with dil. HCl are:

(1) 

(2) 

(3) 

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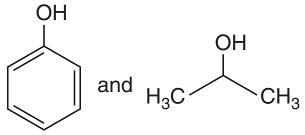
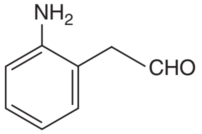


17. The tests performed on compound X and their inferences are:

Test	Inference
(a) 2, 4-DNP test	Coloured precipitate
(b) Iodoform test	Yellow precipitate
(c) Azo-dye test	No dye formation

Compound 'X' is:

(1)


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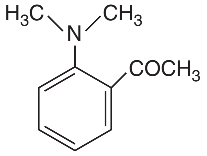

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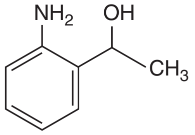

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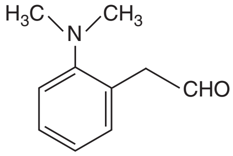


18. If the standard electrode potential for a cell is 2 V at 300 K, the equilibrium constant (K) for the reaction $Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$ at 300 K is approximately

($R = 8\ JK^{-1}\ mol^{-1}$, $F = 96000\ C\ mol^{-1}$)

(1) e^{-80} (2) e^{-160}
(3) e^{320} (4) e^{160}

19. The temporary hardness of water is due to:

(1) Na_2SO_4 (2) NaCl
(3) $Ca(HCO_3)_2$ (4) $CaCl_2$

20. In which of the following processes, the bond order has increased and paramagnetic character has charged to diamagnetic?

(1) $NO \rightarrow NO^+$ (2) $N_2 \rightarrow N_2^+$
(3) $O_2 \rightarrow O_2^+$ (4) $O_2 \rightarrow O_2^{2-}$

21. Which of the following combination of statements is true regarding the interpretation of the atomic orbitals?

(a) An electron in an orbital of high angular momentum stays away from the nucleus than an electron in the orbital of lower angular momentum.

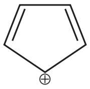
(b) For a given value of the principal quantum number, the size of the orbit is inversely proportional to the azimuthal quantum number.

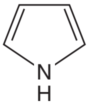
(c) According to wave mechanics, the ground state angular momentum is equal to $\frac{h}{2\pi}$.

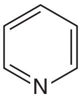
(d) The plot of ψ Vs r for various azimuthal quantum numbers, shows peak shifting towards higher r value.

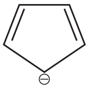
(1) (a), (d) (2) (a), (b)
(3) (a), (c) (4) (b), (c)

22. Which of the following compounds is not aromatic?

(1)


(2)


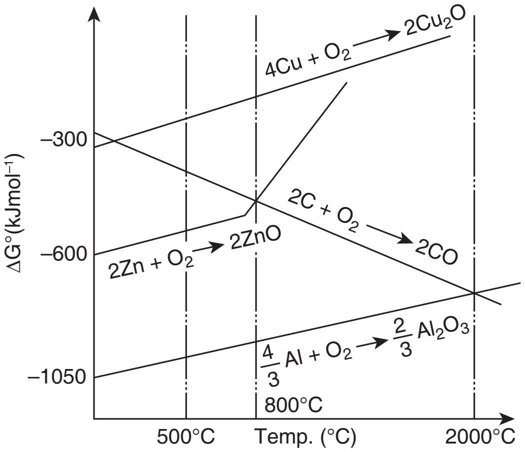
(3)


(4)


23. Good reducing nature of H_3PO_2 is attributed to the presence of:

(1) Two P – OH bonds (2) One P – H bond
(3) Two P – H bonds (4) One P – OH bond

24. The correct statement regarding the given Ellingham diagram is:



(1) At 1400°C, Al can be used for the extraction of Zn from ZnO.

(2) At 500°C, coke can be used for the extraction of Zn from ZnO.

(3) Coke cannot be used for the extraction of Cu from Cu_2O.

(4) At 800°C, Cu can be used for the extraction of Zn from ZnO.

25. The transition element that has lowest enthalpy of atomization, is:

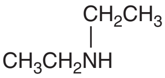
(1) Fe (2) Cu

(3) V (4) Zn

26. The increasing basicity order of the following compounds is:

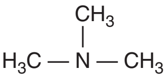
(A) $CH_3CH_2NH_2$

(B)



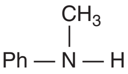
$(CH_3CH_2)NH(CH_2CH_3)$

(C)



$H_3C-N(CH_3)-CH_3$

(D)



$Ph-N(CH_3)-H$

(1) (D) < (C) < (B) < (A)

(2) (D) < (C) < (A) < (B)

(3) (A) < (B) < (C) < (D)

(4) (A) < (B) < (D) < (C)

27. When the first electron gain enthalpy ($\Delta_{eg}H$) of oxygen is −141 $kJmol^{-1}$, its second electron gain enthalpy is:

(1) a more negative value than the first

(2) almost the same as that of the first

(3) negative, but less negative than the first

(4) a positive value

28. At 100°C, copper (Cu) has FCC unit cell structure with cell edge length of x Å. What is the approximate density of Cu (in g cm^{-3}) at this temperature?

[Atomic Mass of Cu = 63.55 u]

(1) $\frac{205}{x^3}$ (2) $\frac{105}{x^3}$

(3) $\frac{211}{x^3}$ (4) $\frac{422}{x^3}$

29. A solution containing 62 g ethylene glycol in 250 g water is cooled to −10°C. If K_f for water is 1.86 K kg mol^{-1}, the amount of water (in g) separated as ice is:

(1) 48 (2) 32

(3) 64 (4) 16

30. Homoleptic octahedral complexes of a metal ion 'M^{3+}' with three monodentate ligands L_1, L_2 and L_3 absorb wavelengths in the region of green, blue and red respectively. The increasing order of the ligand strength is:

(1) $L_3 < L_1 < L_2$ (2) $L_3 < L_2 < L_1$

(3) $L_1 < L_2 < L_3$ (4) $L_2 < L_1 < L_3$

JEE Main 2019 (January 10, Shift 1)

CHEMISTRY

1. The total number of isomers for a square planar complex [M(F)(Cl)(SCN)(NO_2)] is:

(1) 16 (2) 8

(3) 4 (4) 12

2. A process has $\Delta H = 200$ J mol^{-1} and $\Delta S = 40$ JK^{-1} mol^{-1}. Out of the values given below, choose the minimum temperature above which the process will be spontaneous:

(1) 20 K (2) 12 K

(3) 5 K (4) 4 K

3. The values of K_p/K_C for the following reactions at 300 K are, respectively : (At 300 K, $RT = 24.62$ dm^3 atm mol^{-1})

$$N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g)$$
$$N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$$
$$N_2(g) + 3H_2(g) \rightleftharpoons 2\,NH_3(g)$$

(1) 1, 24.62 dm^3 atm mol^{-1}, 606.0 dm^6 atm^2 mol^{-2}

(2) 1, 24.62 dm^3 atm mol^{-1}, 1.65×10^{-3} dm^{-6} atm^{-2} mol^2

(3) 1, 4.1×10^{-2} dm^{-3} atm^{-1} mol, 606 dm^6 atm^2 mol^{-2}

(4) 24.62 dm^3 atm mol^{-1}, 606.0 dm^6 atm^2 mol^{-2}, 1.65×10^{-3} dm^{-6} atm^{-2} mol^2

4. The total number of isotopes of hydrogen and number of radioactive isotopes among them, respectively, are:

(1) 3 and 1 (2) 3 and 2

(3) 2 and 1 (4) 2 and 0

5. Water filled in two glasses A and B have BOD values of 10 and 20, respectively. The correct statement regarding them, is:

(1) B is more polluted than A.

(2) A is suitable for drinking, whereas B is not.

(3) Both A and B are suitable for drinking.

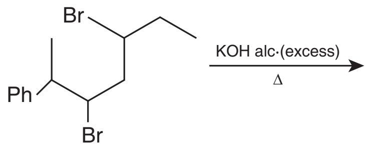
(4) A is more polluted than B.

6. Which primitive unit cell has unequal edge lengths ($a \neq b \neq c$) and all axial angles different from 90°?

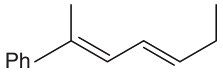
(1) Triclinic (2) Hexagonal

(3) Monoclinic (4) Tetragonal

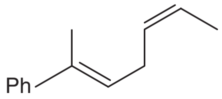
7. The major product of the following reaction is:



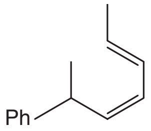
(1)



(2)



(3)



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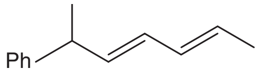
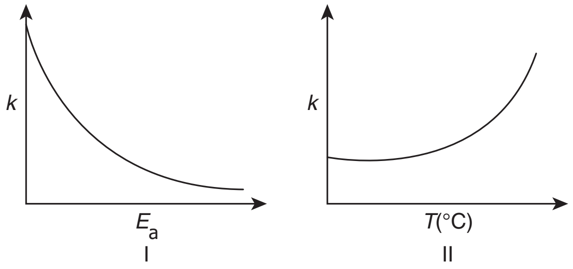


8. Consider the given plots for a reaction obeying Arrhenius equation (0°C < T < 300°C) : (k and E_a are rate constant and activation energy, respectively)



Choose the correct option:

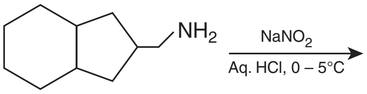
(1) I is right but II is wrong

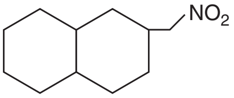
(2) Both I and II are correct

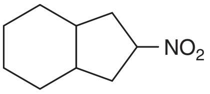
(3) I is wrong but II is right

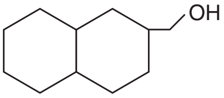
(4) Both I and II are wrong

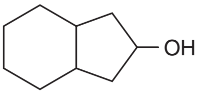
9. The major product formed in the reaction given below will be:



(1)


(2)


(3)


(4)


10. Wilkinson catalyst is:

(1) $[(Ph_3P)_3IrCl]$

(2) $[(Et_3P)_3RhCl]$

(3) $[(Ph_3P)_3RhCl]$ $(Et = C_2H_5)$

(4) $[(Et_3P)_3IrCl]$

11. If dichloromethane (DCM) and water (H_2O) are used for differential extraction, which one of the following statements is correct?

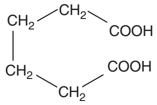
(1) DCM and H_2O would stay as lower and upper layer respectively in the S.F.

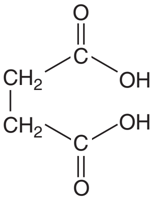
(2) DCM and H_2O will make turbid/colloidal mixture

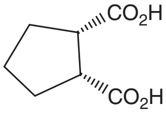
(3) DCM and H_2O would stay as upper and lower layer respectively in the separating funnel (S.F.)

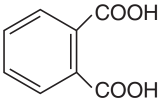
(4) DCM and H_2O will be miscible clearly

12. Which dicarboxylic acid in presence of a dehydrating agent is least reactive to give an anhydride?

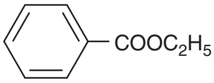
(1)


(2)


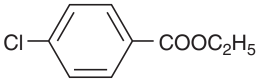
(3)


(4)


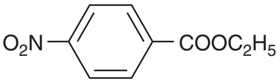
13. The decreasing order of ease of alkaline hydrolysis for the following esters is



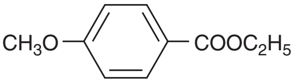
I



II



III

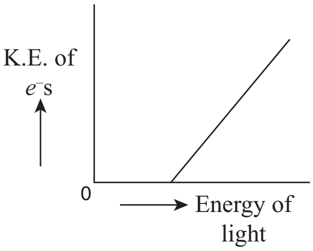


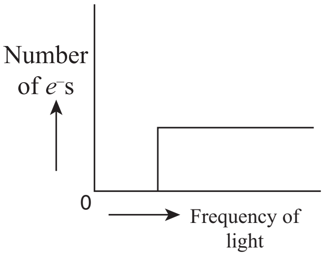
IV

(1) III > II > IV > I (2) III > II > I > IV

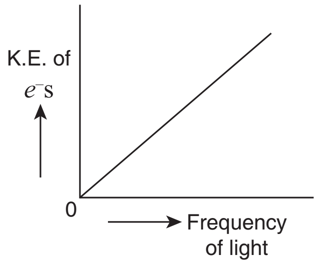
(3) IV > II > III > I (4) II > III > I > IV

14. Which of the graphs shown below does not represent the relationship between incident light and the electron ejected from metal surface?

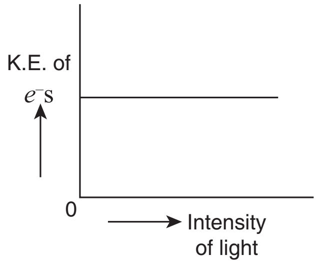
(1)


(2)


(3)



(4)



15. Which of the following is not an example of heterogeneous catalytic reaction?

(1) Ostwald's process

(2) Combustion of coal

(3) Hydrogenation of vegetable oils

(4) Haber's process

16. The effect of lanthanoid contraction in the lanthanoid series of elements by and large means:

(1) increase in both atomic and ionic radii

(2) decrease in atomic radii and increase in ionic radii

(3) decrease in both atomic and ionic radii

(4) increase in atomic radii and decrease in ionic radii

17. Which hydrogen in compound (E) is easily replaceable during bromination reaction in presence of light?

$$\begin{array}{cccc} CH_3- & CH_2- & CH= & CH_2 \\ \delta & \gamma & \beta & \alpha \end{array}$$

(E)

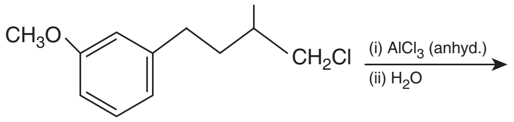
(1) α-hydrogen

(2) γ-hydrogen

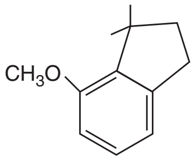
(3) δ-hydrogen

(4) β-hydrogen

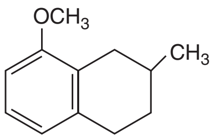
18. The major product of the following reaction is:



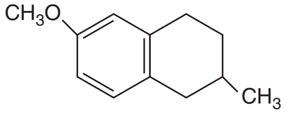
(1)



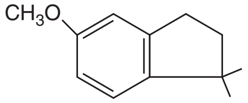
(2)



(3)



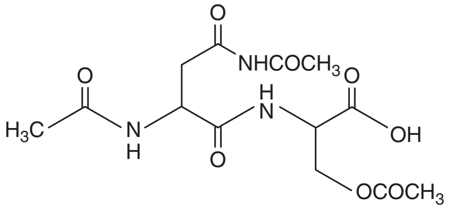
(4)



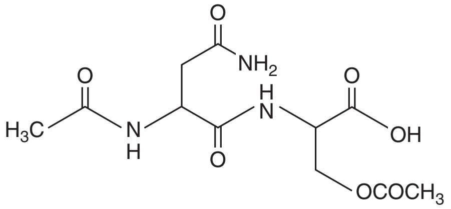
19. The correct structure of product 'P' in the following reaction is:

$$\text{Asn}-\text{Ser}+\underset{\text{(excess)}}{(CH_3CO)_2O}\xrightarrow{NEt_3}P$$

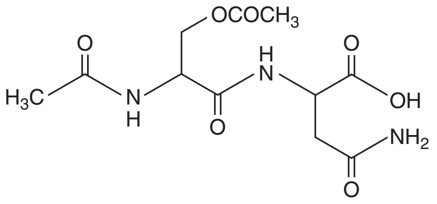
(1)



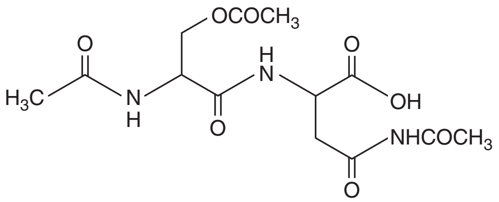
(2)



(3)



(4)



20. The type of hybridisation and number of lone pair(s) of electrons of Xe in $XeOF_4$, respectively, are:

(1) sp^3d^2 and 1
(2) sp^3d and 2
(3) sp^3d^2 and 2
(4) sp^3d and 1

21. The electronegativity of aluminium is similar to:

(1) carbon
(2) beryllium
(3) boron
(4) lithium

22. Consider the following reduction processes:

$$Zn^{2+} + 2e^- \rightarrow Zn(s);\ E^\circ = -0.76\ V$$
$$Ca^{2+} + 2e^- \rightarrow Ca(s);\ E^\circ = -2.87\ V$$
$$Mg^{2+} + 2e^- \rightarrow Mg(s);\ E^\circ = -2.36\ V$$
$$Ni^{2+} + 2e^- \rightarrow Ni(s);\ E^\circ = -0.25\ V$$

The reducing power of the metals increases in the order:

(1) Ca < Zn < Mg < Ni
(2) Ni < Zn < Mg < Ca
(3) Zn < Mg < Ni < Ca
(4) Ca < Mg < Zn < Ni

23. The chemical nature of hydrogen peroxide is:

(1) Oxidising agent in acidic medium, but not in basic medium.
(2) Reducing agent in basic medium, but not in acidic medium.
(3) Oxidising and reducing agent in acidic medium, but not in basic medium.
(4) Oxidising and reducing agent in both acidic and basic medium.

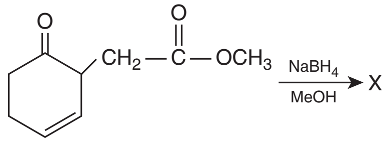
24. A mixture of 100 m mol of $Ca(OH)_2$ and 2 g of sodium sulphate was dissolved in water and the volume was made up to 100 mL. The mass of calcium sulphate formed and the concentration of OH^- in resulting solution, respectively, are: (Molar mass of $Ca(OH)_2$, Na_2SO_4 and $CaSO_4$ are 74, 143 and 136 g mol^{-1}, respectively; K_{sp} of $Ca(OH)_2$ is 5.5×10^{-6})

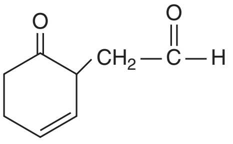
(1) 1.9 g, 0.28 mol L^{-1}
(2) 13.6 g, 0.28 mol L^{-1}
(3) 1.9 g, 0.14 mol L^{-1}
(4) 13.6 g, 0.14 mol L^{-1}

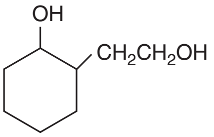
25. Liquids A and B form an ideal solution in the entire composition range. At 350 K, the vapor pressures of pure A and B are 7×10^3 Pa and 12×10^3 Pa, respectively. The composition of the vapor in equilibrium with a solution containing 40 mol percent of A at this temperature is:

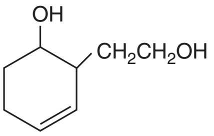
(1) $x_A = 0.37; x_B = 0.63$
(2) $x_A = 0.28; x_B = 0.72$
(3) $x_A = 0.4; x_B = 0.6$
(4) $x_A = 0.76; x_B = 0.24$

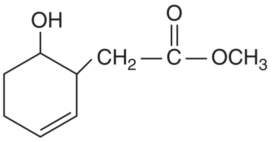
26. The major product 'X' formed in the following reaction is:



(1)


(2)


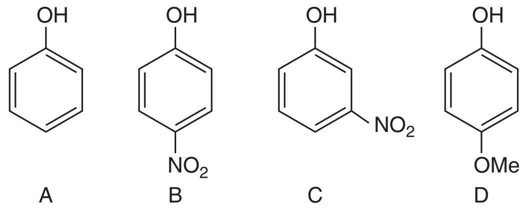
(3)


(4)


27. The metal used for making X-ray tube window is:

(1) Mg
(2) Na
(3) Be
(4) Ca

28. The increasing order of the pK_a values of the following compounds is:



(1) C < B < A < D
(2) B < C < D < A
(3) D < A < C < B
(4) B < C < A < D

29. Hall-Heroult's process is given by:

(1) $Cu^{2+}(aq) + H_2(g) \rightarrow Cu(s) + 2H^+(aq)$
(2) $Cr_2O_3 + 2\,Al \rightarrow Al_2O_3 + 2\,Cr$
(3) $2\,Al_2O_3 + 3\,C \rightarrow 4\,Al + 3\,CO_2$
(4) $ZnO + C \xrightarrow{\text{Coke, 1673 K}} Zn + CO$

30. Two π and half σ bonds are present in:

(1) O_2^+
(2) N_2
(3) O_2
(4) N_2^+

JEE Main 2019 (January 10, Shift 2)

CHEMISTRY

1. The ground state energy of hydrogen atom is −13.6 eV. The energy of second excited state of He^+ ion in eV is:

(1) −54.4 (2) −3.4

(3) −6.04 (4) −27.2

2. Haemoglobin and gold sol are examples of:

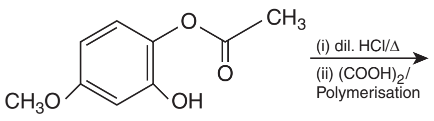
(1) positively and negatively charged sols, respectively

(2) positively charged sols

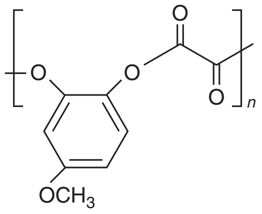
(3) negatively charged sols

(4) negatively and positively charged sols, respectively

3. The major product of the following reaction is:



(1)



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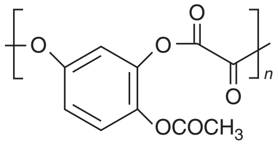

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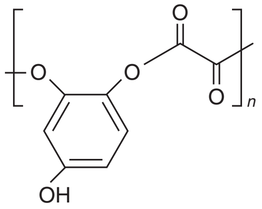

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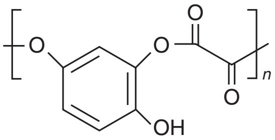


4. The amount of sugar ($C_{12}H_{22}O_{11}$) required to prepare 2 L of its 0.1 M aqueous solution is:

(1) 136.8 g (2) 17.1 g

(3) 68.4 g (4) 34.2 g

5. Among the following reactions of hydrogen with halogens, the one that requires a catalyst is:

(1) $H_2 + I_2 \rightarrow 2\,HI$ (2) $H_2 + Cl_2 \rightarrow 2\,HCl$

(3) $H_2 + Br_2 \rightarrow 2\,HBr$ (4) $H_2 + F_2 \rightarrow 2\,HF$

6. 5.1 g of NH_4SH is introduced in 3.0 L evacuated flask at 327°C. 30% of the solid NH_4SH decomposed to NH_3 and H_2S as gases. The K_p of the reaction at 327°C is (R = 0.082 L atm mol^{-1} K^{-1}, Molar mass of S = 32 g mol^{-1}, molar mass of N = 14 g mol^{-1})

(1) 0.242×10^{-4} atm^2 (2) 1×10^{-4} atm^2

(3) 4.9×10^{-3} atm^2 (4) 0.242 atm^2

7. The reaction that is **NOT** involved in the ozone layer depletion mechanism in the stratosphere is:

(1) $CF_2Cl_2(g) \xrightarrow{UV} \dot{C}l(g) + \dot{C}F_2Cl(g)$

(2) $Cl\dot{O}(g) + O(g) \rightarrow \dot{C}l(g) + O_2(g)$

(3) $CH_4 + 2\,O_3 \rightarrow 3\,CH_2 = O + 3\,H_2O$

(4) $HOCl(g) \xrightarrow{h\nu} \dot{O}H(g) + \dot{C}l(g)$

8. In the cell $Pt(s)|H_2(g, 1\,bar)|HCl(aq)|AgCl(s)|Ag(s)|Pt(s)$ the cell potential is 0.92 V when a 10^{-6} molal HCl solution is used. The standard electrode potential of ($AgCl/Ag, Cl^-$) electrode is:

$$\left\{\text{Given, } \frac{2.303RT}{F} = 0.06 \text{ V at } 298 \text{ K}\right\}$$

(1) 0.94 V (2) 0.76 V
(3) 0.40 V (4) 0.20 V

9. The 71st electron of an element X with an atomic number of 71 enters into the orbital:

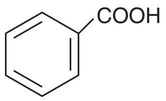
(1) 6*p* (2) 4*f*
(3) 5*d* (4) 6*s*

10. The correct match between item 'I' and item 'II' is

Item 'I'	**Item 'II'**
(compound)	(reagent)
(A) Lysine	(P) 1-naphthol
(B) Furfural	(Q) ninhydrin
(C) Benzyl alcohol	(R) $KMnO_4$
(D) Styrene	(S) Ceric ammonium nitrate

(1) (A) → (Q); (B) → (P); (C) → (S); (D) → (R)
(2) (A) → (Q); (B) → (P); (C) → (R); (D) → (S)
(3) (A) → (R); (B) → (P); (C) → (Q); (D) → (S)
(4) (A) → (Q); (B) → (R); (C) → (S); (D) → (P)

11. An aromatic compound 'A' having molecular formula $C_7H_6O_2$ on treating with aqueous ammonia and heating forms compound 'B'. The compound 'B' on reaction with molecular bromine and potassium hydroxide provides compound 'C' having molecular formula C_6H_7N. The structure of 'A' is:

(1)


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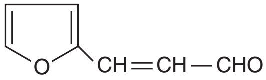

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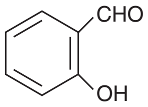

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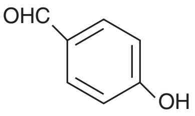


12. The process with negative entropy change is:

(1) Dissociation of $CaSO_4(s)$ to $CaO(s)$ and $SO_3(g)$
(2) Sublimation of dry ice
(3) Dissolution of iodine in water
(4) Synthesis of ammonia from N_2 and H_2

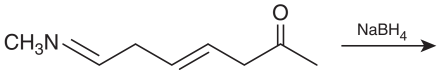
13. An ideal gas undergoes isothermal compression from 5 m^3 to 1 m^3 against a constant external pressure of 4 Nm^{-2}. Heat released in this process is used to increase the temperature of 1 mole of Al. If molar heat capacity of Al is 24 J mol^{-1} K^{-1}, the temperature of Al increases by:

(1) $\frac{3}{2}$K (2) 2 K
(3) $\frac{2}{3}$K (4) 1 K

14. Elevation in the boiling point for 1 molal solution of glucose is 2 K. The depression in the freezing point for 2 molal solution of glucose in the same solvent is 2 K. The relation between K_b and K_f is:

(1) $K_b = 1.5\ K_f$ (2) $K_b = K_f$
(3) $K_b = 0.5\ K_f$ (4) $K_b = 2\ K_f$

15. The major product of the following reaction is:



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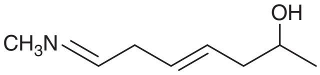

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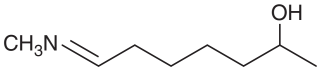

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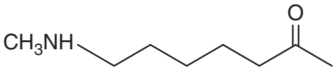

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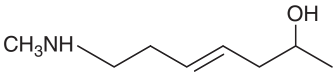


16. Sodium metal on dissolution in liquid ammonia gives a deep blue solution due to the formation of:

(1) sodium-ammonia complex
(2) sodamide
(3) sodium ion-ammonia complex
(4) ammoniated electrons

17. For an elementary chemical reaction, $A_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2A$, the expression for $\frac{d[A]}{dt}$ is:

(1) $k_1[A_2] - k_{-1}[A]^2$ (2) $2k_1[A_2] - k_{-1}[A]^2$
(3) $k_1[A_2] + k_{-1}[A]^2$ (4) $2k_1[A_2] - 2k_{-1}[A]^2$

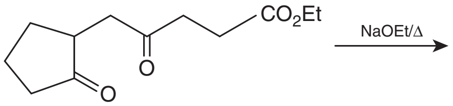
18. Which of the following tests cannot be used for identifying amino acids?

(1) Biuret test (2) Barfoed test
(3) Ninhydrin test (4) Xanthoproteic test

19. The difference in the number of unpaired electrons of a metal ion in its high-spin and low-spin octahedral complexes is two. The metal ion is:

(1) Ni^{2+} (2) Fe^{2+}
(3) Co^{2+} (4) Mn^{2+}

20. The major product obtained in the following reaction is:



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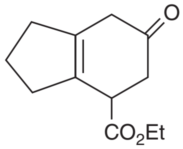

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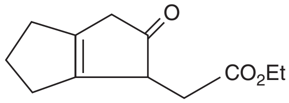

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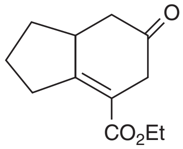

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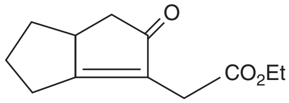
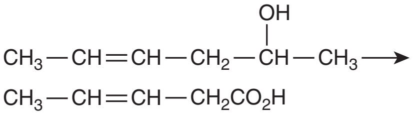


21. The pair that contains two P – H bonds in each of the oxoacids is:

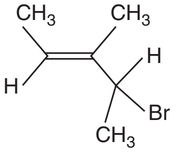
(1) $H_4P_2O_5$ and $H_4P_2O_6$ (2) H_3PO_2 and $H_4P_2O_5$
(3) H_3PO_3 and H_3PO_2 (4) $H_4P_2O_5$ and H_3PO_3

22. Which is the most suitable reagent for the following transformation?


$$CH_3-CH=CH-CH_2-\overset{OH}{\overset{|}{C}H}-CH_3 \longrightarrow$$
$$CH_3-CH=CH-CH_2CO_2H$$

(1) Tollens' reagent (2) I_2/NaOH
(3) CrO_2Cl_2/CS_2 (4) alkaline $KMnO_4$

23. What is the IUPAC name of the following compound?



(1) 3-Bromo-1, 2-dimethylbut-1-ene
(2) 3-Bromo-3-methyl-1, 2-dimethylprop-1-ene
(3) 2-Bromo-3-methylpent-3-ene
(4) 4-Bromo-3-methylpent-2-ene

24. The number of 2-centre-2-electron and 3-centre-2-electron bonds in B_2H_6, respectively, are:

(1) 2 and 1 (2) 4 and 2
(3) 2 and 2 (4) 2 and 4

25. In the reaction of oxalate with permanganate in acidic medium, the number of electrons involved in producing one molecule of CO_2 is:

(1) 1 (2) 10
(3) 2 (4) 5

26. A reaction of cobalt(III) chloride and ethylenediamine in a 1 : 2 mole ratio generates two isomeric products A (violet coloured) and B (green coloured). A can show optical activity, but, B is optically inactive. What type of isomers does A and B represent?

(1) Geometrical isomers (2) Coordination isomers
(3) Linkage isomers (4) Ionisation isomers

27. The electrolytes usually used in the electroplating of gold and silver, respectively, are:

(1) $[Au(CN)_2]^-$ and $[Ag(CN)_2]^-$
(2) $[Au(CN)_2]^-$ and $[AgCl_2]^-$
(3) $[Au(OH)_4]^-$ and $[Ag(OH)_2]^-$
(4) $[Au(NH_3)_2]^+$ and $[Ag(CN)_2]^-$

28. A compound of formula A_2B_3 has the hcp lattice. Which atom forms the hcp lattice and what fraction of tetrahedral voids is occupied by the other atoms:

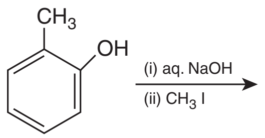
(1) hcp lattice – A, $\frac{2}{3}$ tetrahedral voids – B

(2) hcp lattice – A, $\frac{1}{3}$ tetrahedral voids – B

(3) hcp lattice – B, $\frac{2}{3}$ tetrahedral voids – A

(4) hcp lattice – B, $\frac{1}{3}$ tetrahedral voids – A

29. The major product of the following reaction is:



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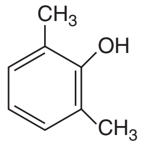

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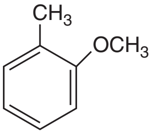

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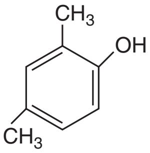

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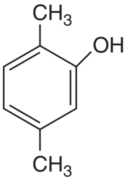
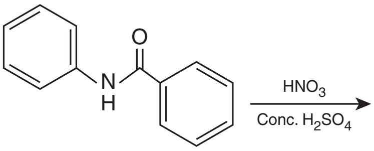
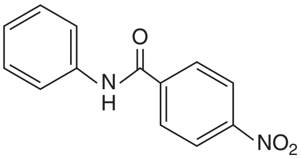


30. What will be the major product in the following mononitration reaction?



(1)



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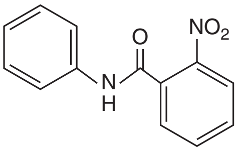

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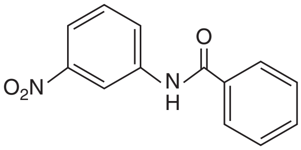

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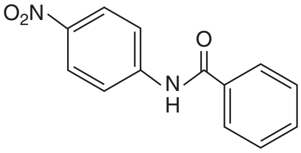
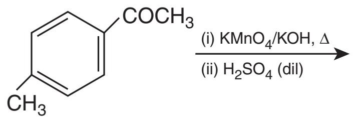
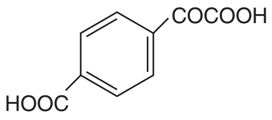


JEE Main 2019 (January 11, Shift 1)

CHEMISTRY

1. The major product of the following reaction is



(1)


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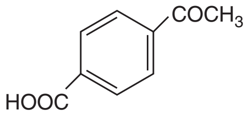

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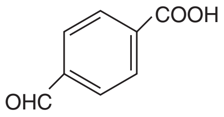

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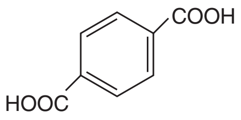


2. The **correct** statements among (a) to (d) regarding H_2 as a fuel are:

(a) It produces less pollutants than petrol.

(b) A cylinder of compressed dihydrogen weighs ~30 times more than a petrol tank producing the same amount of energy.

(c) Dihydrogen is stored in tanks of metal alloys like $NaNi_5$.

(d) On combustion, values of energy released per gram of liquid dihydrogen and LPG are 50 and 142 kJ, respectively.

(1) (a) and (c) only
(2) (b) and (d) only
(3) (b), (c) and (d) only
(4) (a), (b) and (c) only

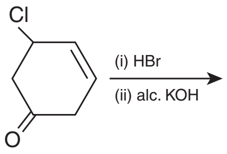
3. An organic compound is estimated through Dumus method and was found to evolve 6 moles of CO_2, 4 moles of H_2O and 1 mole of nitrogen gas. The formula of the compound is:

(1) $C_{12}H_8N_2$
(2) $C_{12}H_8N$
(3) $C_6H_8N_2$
(4) C_6H_8N

4. An example of solid sol is:

(1) butter
(2) paint
(3) hair cream
(4) gem stones

5. The major product of the following reaction is:



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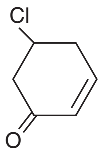

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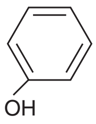

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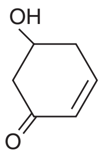

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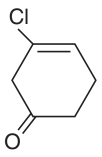
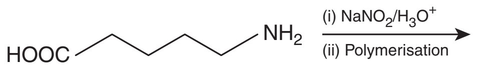


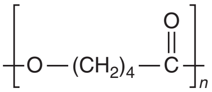
6. Heat treatment of muscular pain involves radiation of wavelength of about 900 nm. Which spectral line of H-atom is suitable for this purpose ?

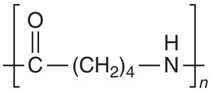
$[R_H = 1 \times 10^5\ cm^{-1},\ h = 6.6 \times 10^{-34}\ Js,\ c = 3 \times 10^8\ ms^{-1}]$

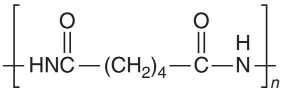
(1) Balmer, $\infty \rightarrow 2$
(2) Paschen, $5 \rightarrow 3$
(3) Lyman, $\infty \rightarrow 1$
(4) Paschen, $\infty \rightarrow 3$

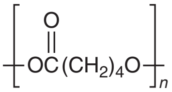
7. The polymer obtained from the following reactions is:



(1) 
$\left[O-(CH_2)_4-\overset{O}{\overset{\|}{C}} \right]_n$

(2) 
$\left[\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{H}{N} \right]_n$

(3) 
$\left[HN\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-\overset{H}{N} \right]_n$

(4) 
$\left[O\overset{O}{\overset{\|}{C}}(CH_2)_4O \right]_n$

8. NaH is an example of:

(1) saline hydride

(2) metallic hydride

(3) molecular hydride

(4) electron-rich hydride

9. Consider the reaction

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

The equilibrium constant of the above reaction is K_p. If pure ammonia is left to dissociate, the partial pressure of ammonia at equilibrium is given by (Assume that $p_{NH_3} << p_{total}$ at equilibrium)

(1) $\frac{3^{3/2} K_p^{1/2} p^2}{4}$ (2) $\frac{3^{3/2} K_p^{1/2} p^2}{16}$

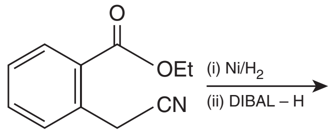
(3) $\frac{K_p^{1/2} p^2}{4}$ (4) $\frac{K_p^{1/2} p^2}{16}$

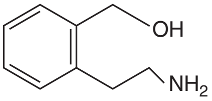
10. The chloride that CANNOT get hydrolysed is:

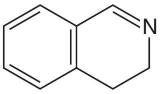
(1) CCl_4 (2) $PbCl_4$

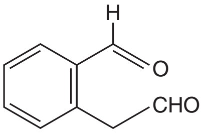
(3) $SnCl_4$ (4) $SiCl_4$

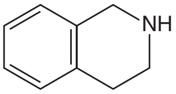
11. The major product of the following reaction is:



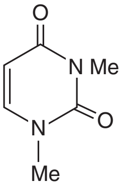
(1) 

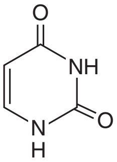
(2) 

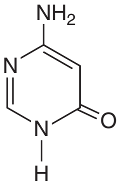
(3) 

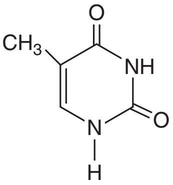
(4) 

12. Among the following compounds, which one is found in RNA?

(1) 

(2) 

(3) 

(4) 

13. Peroxyacetyl nitrate (PAN), an eye irritant is produced by:

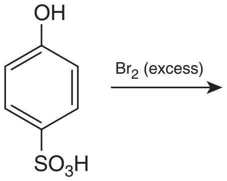
(1) photochemical smog

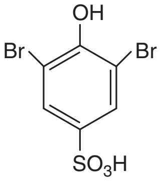
(2) organic waste

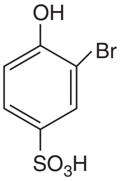
(3) acid rain

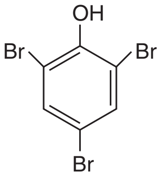
(4) classical smog

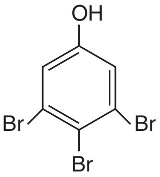
14. The major product of the following reaction is:



(1) 

(2) 

(3) 

(4) 

15. If a reaction follows the Arrhenius equation, the plot ln*k* vs 1/(*RT*) gives straight line with a gradient (−*y*) unit. The energy required to activate the reactant is:

(1) y unit (2) y/R unit

(3) $-y$ unit (4) yR unit

16. The correct match between item (I) and item (II) is:

Item - I	**Item - II**
(A) Norethindrone	(P) Anti-biotic
(B) Ofloxacin	(Q) Anti-fertility
(C) Equanil	(R) Hypertension
	(S) Analgesics

(1) (A) → (R); (B) → (P); (C) → (S)

(2) (A) → (Q); (B) → (P); (C) → (R)

(3) (A) → (Q); (B) → (R); (C) → (S)

(4) (A) → (R); (B) → (P); (C) → (R)

17. For the chemical reaction $X \rightleftharpoons Y$, the standard reaction Gibbs energy depends on temperature T (in K) as

$$\Delta_r G^\circ \text{ (in kJ mol}^{-1}) = 120 - \frac{3}{8}T.$$

The major component of the reaction mixture at T is:

(1) Y if $T = 300$ K (2) Y if $T = 280$ K

(3) X if $T = 315$ K (4) X if $T = 350$ K

18. The element that usually does NOT show variable oxidation states is:

(1) Sc (2) V

(3) Ti (4) Cu

19. Match the ores (List I) with the metals (List II):

(List I)	**(List II)**
Ores	**Metals**
(A) Siderite	(P) Zinc
(B) Kaolinite	(Q) Copper
(C) Malachite	(R) Iron
(D) Calamine	(S) Aluminium

(1) (A) → (R); (B) → (S); (C) → (P); (D) → (Q)

(2) (A) → (P); (B) → (Q); (C) → (R); (D) → (S)

(3) (A) → (Q); (B) → (R); (C) → (S); (D) → (P)

(4) (A) → (R); (B) → (S); (C) → (Q); (D) → (P)

20. The correct match between items I and II is:

Item - I	**Item - II**
(Mixture)	**(Seperation method)**
(A) H_2O: Sugar	(P) Sublimation
(B) H_2O: Aniline	(Q) Recrystallization
(C) H_2O: Toluene	(R) Steam distillation
	(S) Differential extraction

(1) (A) → (R); (B) → (P); (C) → (S)

(2) (A) → (Q); (B) → (R); (C) → (S)

(3) (A) → (S); (B) → (R); (C) → (P)

(4) (A) → (Q); (B) → (R); (C) → (P)

21. The freezing point of a diluted milk sample is found to be −0.2°C, while it should have been −0.5° C for pure milk. How much water has been added to pure milk to make the diluted sample?

(1) 1 cup of water to 2 cups of pure milk

(2) 2 cups of water to 3 cups of pure milk

(3) 3 cups of water to 2cups of pure milk

(4) 1 cup of water to 3 cups of pure milk

22. For the cell $Zn(s)|Zn^{2+}(aq)||M^{x+}(aq)|M(s)$, different half cells and their standard electrode potentials are given below:

M^{x+} (aq)/ M(s)	Au^{3+} (aq)/ Au(s)	Ag^{+} (aq)/ Ag(s)	Fe^{3+} (aq)/ Fe^{2+} (aq)	Fe^{2+} (aq)/ Fe(s)
$E^\circ_{M^{x+}/M}$/(V)	1.40	0.80	0.77	−0.44

If $E^\circ_{Zn^{2+}/Zn} = -0.76$ V, which cathode will give a maximum value of E°_{cell} per electron transferred?

(1) Ag^+/Ag (2) Au^{3+}/Au

(3) Fe^{3+}/Fe^{2+} (4) Fe^{2+}/Fe

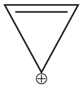
23. A 10 mg effervescent tablet containing sodium bicarbonate and oxalic acid releases 0.25 mL of CO_2 at $T = 298.15$ K and $p = 1$ bar. If molar volume of CO_2 is 25.0 L under such condition, what is the percentage of sodium bicarbonate in each tablet?

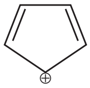
[Molar mass of $NaHCO_3$ = 84 g mol^{-1}]

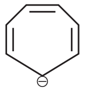
(1) 33.6 (2) 8.4

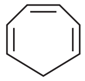
(3) 16.8 (4) 0.84

24. Which compound (s) out of the following is/are not aromatic?


(A)


(B)


(C)


(D)

(1) (A) and (C) (2) (B), (C) and (D)

(3) (C) and (D) (4) (B)

25. The correct order of the atomic radii of C, Cs, Al, and S is:

(1) C < S < Cs < Al

(2) S < C < Al < Cs

(3) C < S < Al < Cs

(4) S < C < Cs < Al

26. Match the metals (List I) with the coordination compound(s)/enzyme(s) (List II):

(List I) **Metals**	**(List II)** **Coordination Compound(s)/Enzyme(s)**
(A) Co	(P) Wilkinson catalyst
(B) Zn	(Q) Chlorophyll
(C) Rh	(R) Vitamin B_{12}
(D) Mg	(S) Carbonic anhydrase

(1) (A) → (R); (B) → (S); (C) → (P); (D) → (Q)
(2) (A) → (Q); (B) → (P); (C) → (S); (D) → (R)
(3) (A) → (P); (B) → (Q); (C) → (R); (D) → (S)
(4) (A) → (S); (B) → (R); (C) → (P); (D) → (Q)

27. Two blocks of the same metal having same mass and at temperature T_1 and T_2, respectively, are brought in contact with each other and allowed to attain thermal equilibrium at constant pressure. The change in entropy, ΔS, for this process is:

(1) $2C_p \ln\left[\frac{(T_1+T_2)^{\frac{1}{2}}}{T_1T_2}\right]$ (2) $C_p \ln\left[\frac{(T_1+T_2)^2}{4T_1T_2}\right]$

(3) $2C_p \ln\left[\frac{T_1+T_2}{2T_1T_2}\right]$ (4) $2C_p \ln\left[\frac{T_1+T_2}{4T_1T_2}\right]$

28. The amphoteric hydroxide is:

(1) $Sr(OH)_2$ (2) $Mg(OH)_2$
(3) $Ca(OH)_2$ (4) $Be(OH)_2$

29. A solid having density of 9×10^3 kg m^{-3} forms face centred cubic crystals of edge length $200\sqrt{2}$ pm. What is the molar mass of the solid?

[Avogadro constant $\cong$ 6×10^{23} mol^{-1}, $\pi = 3$]

(1) 0.0432 kg mol^{-1} (2) 0.0305 kg mol^{-1}
(3) 0.0216 kg mol^{-1} (4) 0.4320 kg mol^{-1}

30. The concentration of dissolved oxygen (DO) in cold water can go upto:

(1) 10 ppm (2) 8 ppm
(3) 14 ppm (4) 16 ppm

JEE Main 2019 (January 11, Shift 2)

CHEMISTRY

1. The reaction, $MgO(s) + C(s) \rightarrow Mg(s) + CO(g)$, for which $\Delta_r H^\circ = +491.1$ kJ mol^{-1} and $\Delta_r S^\circ = 198.0$ JK^{-1} mol^{-1}, is not feasible at 298 K. Temperature above which reaction will be feasible is:

(1) 2040.5 K (2) 1890.0 K

(3) 2480.3 K (4) 2380.5 K

2. The **correct** match between Item I and Item II is:

Item I	**Item II**
(A) Allosteric effect	(P) Molecule binding to the active site of enzyme
(B) Competitive inhibitor	(Q) Molecule crucial for communication in the body
(C) Receptor	(R) Molecule binding to a site other than the active site of enzyme
(D) Poison	(S) Molecule binding to the enzyme covalently

(1) (A) →(R); (B) → (P); (C) → (Q); (D) → (S)

(2) (A) → (P); (B) → (R); (C) → (Q); (D) → (S)

(3) (A) → (R); (B) → (P); (C) → (S); (D) → (Q)

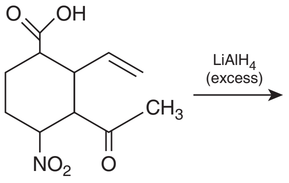
(4) (A) → (P); (B) → (R); (C) → (S); (D) → (Q)

3. The coordination number of Th in $K_4[Th(C_2O_4)_4(OH_2)_2]$ is: $\left(C_2O_4^{2-} = \text{Oxalato}\right)$

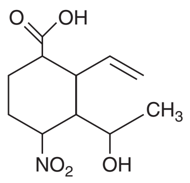
(1) 14 (2) 6

(3) 8 (4) 10

4. The major product obtained in the following reaction is:



(1)



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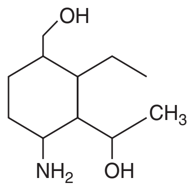

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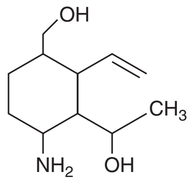
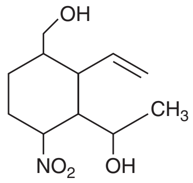


(4)



5. The standard reaction Gibbs energy for a chemical reaction at an absolute temperature T is given by $\Delta_r G^\circ = A - BT$

Where A and B are non-zero constants. Which of the following is **TRUE** about this reaction?

(1) Endothermic if $A > 0$

(2) Exothermic if $A > 0$ and $B < 0$

(3) Endothermic if $A < 0$ and $B > 0$

(4) Exothermic if $B < 0$

6. The radius of the largest sphere which fits properly at the centre of the edge of a body centred cubic unit cell is: (Edge length is represented by '*a*')

(1) 0.027 *a* (2) 0.047 *a*

(3) 0.134 *a* (4) 0.067 *a*

7. The hydride that is NOT electron deficient is:

(1) SiH_4 (2) B_2H_6

(3) GaH_3 (4) AlH_3

8. Given the equilibrium constant: K_C of the reaction:

$Cu(s) + 2Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$ is

10×10^{15}, calculate the E°_{cell} of this reaction at 298 K

$$\left[2.303\frac{RT}{F} \text{ at } 298\text{ K} = 0.059\text{ V}\right]$$

(1) 0.04736 mV (2) 0.4736 mV

(3) 0.4736 V (4) 0.04736 V

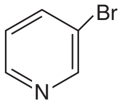
9. The correct option with respect to the Pauling electronegativity values of the elements is:

(1) Te > Se (2) Ga < Ge

(3) Si < Al (4) P > S

10. Which of the following compounds will produce a precipitate with $AgNO_3$?

(1)



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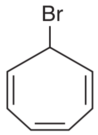

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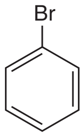

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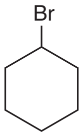


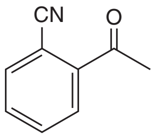
11. The de Broglie wavelength (λ) associated with a photoelectron varies with the frequency (ν) of the incident radiation as, [ν_0 is threshold frequency]:

(1) $\lambda \propto \frac{1}{(\nu - \nu_0)}$ (2) $\lambda \propto \frac{1}{(\nu - \nu_0)^{\frac{1}{4}}}$

(3) $\lambda \propto \frac{1}{(\nu - \nu_0)^{\frac{3}{2}}}$ (4) $\lambda \propto \frac{1}{(\nu - \nu_0)^{\frac{1}{2}}}$

12. Which of the following compounds reacts with ethylmagnesium bromide and also decolourizes bromine water solution:

(1)



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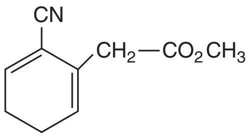
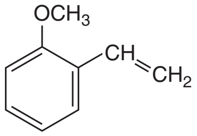
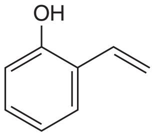


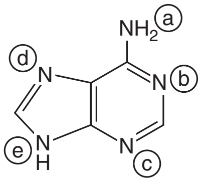
(3)



(4)



13. In the following compound,



the favourable site/s for protonation is/are:

(1) (a) and (e) (2) (b), (c) and (d)

(3) (a) and (d) (4) (a)

14. Taj Mahal is being slowly disfigured and discoloured. This is primarily due to:

(1) global warming (2) acid rain

(3) water pollution (4) soil pollution

15. The relative stability of + 1 oxidation state of Group 13 elements follows the order:

(1) Al < Ga < Tl < In (2) Tl < In < Ga < Al

(3) Ga < Al < In < Tl (4) Al < Ga < In < Tl

16. For the equilibrium, $2H_2O \rightleftharpoons H_3O^+ + OH^-$, the value of ΔG° at 298 K is approximately:

(1) 100 kJ mol^{-1} (2) −80 kJ mol^{-1}

(3) 80 kJ mol^{-1} (4) −100 kJ mol^{-1}

17. The reaction that does NOT define calcination is:

(1) $Fe_2O_3 \cdot XH_2O \xrightarrow{\Delta} Fe_2O_3 \quad XH_2O$

(2) $2Cu_2S + 3O_2 \xrightarrow{\Delta} 2Cu_2O \quad 2SO_2$

(3) $ZnCO_3 \xrightarrow{\Delta} ZnO \quad CO_2$

(4) $CaCO_3 \cdot MgCO_3 \xrightarrow{\Delta} CaO \quad MgO \quad 2CO_2$

18. A compound 'X' on treatment with Br_2/NaOH, provided C_3H_9N, which gives positive carbylamine test. Compound 'X' is:

(1) $CH_3COCH_2NHCH_3$ (2) $CH_3CH_2COCH_2NH_2$

(3) $CH_3CH_2CH_2CONH_2$ (4) $CH_3CON(CH_3)_2$

19. Among the colloids cheese (C), milk (M) and smoke (S), the correct combination of the dispersed phase and dispersion medium, respectively is:

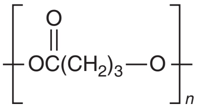
(1) C: liquid in solid; M: liquid in solid; S: solid in gas

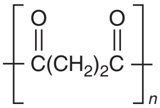
(2) C: liquid in solid; M: liquid in liquid; S: solid in gas

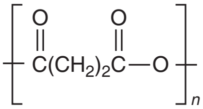
(3) C: solid in liquid; M: liquid in liquid; S: gas in solid

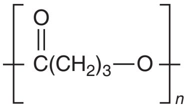
(4) C: solid in liquid; M: solid in liquid; S: solid in gas

20. The homopolymer formed from 4-hydroxy-butanoic acid is:

(1)

$\left[-O\overset{\overset{O}{\|}}{C}(CH_2)_3-O-\right]_n$

(2)

$\left[-\overset{\overset{O}{\|}}{C}(CH_2)_2\overset{\overset{O}{\|}}{C}-\right]_n$

(3)

$\left[-\overset{\overset{O}{\|}}{C}(CH_2)_2\overset{\overset{O}{\|}}{C}-O-\right]_n$

(4)

$\left[-\overset{\overset{O}{\|}}{C}(CH_2)_3-O-\right]_n$

21. K_2HgI_4 is 40% ionised in aqueous solution. The value of its van't Hoff factor (i) is:

(1) 1.6 (2) 1.8

(3) 2.0 (4) 2.2

22. 25 mL of the given HCl solution requires 30 mL of 0.1 M sodium carbonate solution. What is the volume of this HCl solution required to titrate 30 mL of 0.2 M aqueous NaOH solution ?

(1) 25 mL (2) 75 mL

(3) 50 mL (4) 12.5 mL

23. The reaction 2X → B is a zeroth order reaction. If the initial concentration of X is 0.2 M, the half-life is 6 h. When the initial concentration of X is 0.5 M, the time required to reach its final concentration of 0.2 M will be:

(1) 9.0 h (2) 12.0 h

(3) 18.0 h (4) 7.2 h

24. Match the following items in List I with the corresponding items in List II.

List I	**List II**
(A) $Na_2CO_3 \cdot 10\,H_2O$	(P) Portland cement ingredient
(B) $Mg(HCO_3)_2$	(Q) Castner-Kellner process
(C) NaOH	(R) Solvay process
(D) $Ca_3Al_2O_6$	(S) Temporary hardness

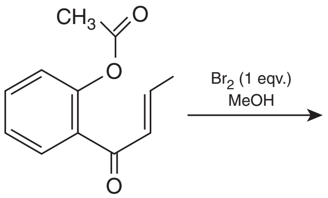
(1) (A) → (Q); (B) → (R); (C) → (P); (D) → (S)

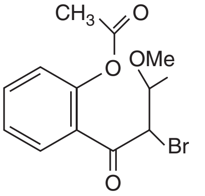
(2) (A) → (R); (B) → (Q); (C) → (S); (D) → (P)

(3) (A) → (S); (B) → (P); (C) → (Q); (D) → (R)

(4) (A) → (R); (B) → (S); (C) → (Q); (D) → (P)

25. The major product obtained in the following conversion is:



(1)


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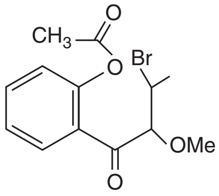
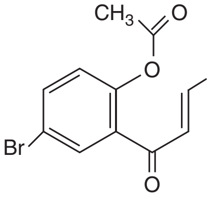
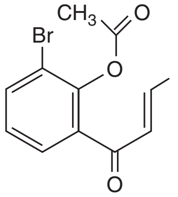
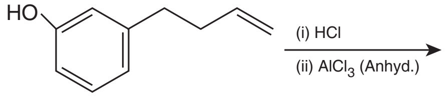
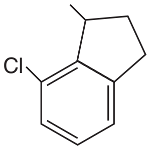


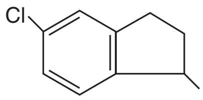
(3)


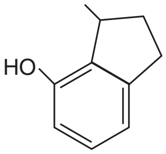
(4)


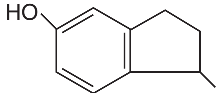
26. Major product of the following reaction is:



(1)


(2)


(3)


(4)


27. The higher concentration of which gas in air can cause stiffness of flower buds?

(1) NO_2 (2) CO_2

(3) SO_2 (4) CO

28. The correct match between Item I and Item II is:

Item I	**Item II**
(A) Ester test	(P) Tyr
(B) Carbylamine test	(Q) Asp
(C) Phthalein dye test	(R) Ser
	(S) Lys

(1) (A) → (Q); (B) → (S); (C) → (P)

(2) (A) → (R); (B) → (Q); (C) → (P)

(3) (A) → (R); (B) → (S); (C) → (Q)

(4) (A) → (Q); (B) → (S); (C) → (R)

29. The number of bridging CO ligand(s) and Co-Co bond(s) in $Co_2(CO)_8$, respectively are:

(1) 2 and 1 (2) 2 and 0

(3) 0 and 2 (4) 4 and 0

30. $\underline{A} \xrightarrow{4KOH,\, O_2} 2\underline{B} + 2H_2O$ (Green)

$3\underline{B} \xrightarrow{4HCl} 2\underline{C} + MnO_2 + 2H_2O$ (Purple)

$2\underline{C} \xrightarrow{H_2O,\, KI} 2\underline{A} + 2\,KOH + \underline{D}$

In the above sequence of reactions, $\underline{A}$ and $\underline{D}$, respectively, are:

(1) KI and $KMnO_4$

(2) MnO_2 and KIO_3

(3) KIO_3 and MnO_2

(4) KI and K_2MnO_4

JEE Main 2019 (January 12, Shift 1)

CHEMISTRY

1. In the Hall-Heroult process, aluminium is formed at the cathode. The cathode is made out of:

(1) Pure aluminium (2) Carbon

(3) Copper (4) Platinum

2. The correct order for acid strength of compounds $CH \equiv CH, CH_3-C \equiv CH$ and $CH_2 = CH_2$ is as follows:

(1) $CH \equiv CH > CH_2 = CH_2 > CH_3 - C \equiv CH$

(2) $CH_3 - C \equiv CH > CH \equiv CH > CH_2 = CH_2$

(3) $CH_3 - C \equiv CH > CH_2 = CH_2 > HC \equiv CH$

(4) $HC \equiv CH > CH_3 - C \equiv CH > CH_2 = CH_2$

3. In a chemical reaction, $A + 2B \overset{K}{\rightleftharpoons} 2C + D$, the initial concentration of B was 1.5 times of the concentration of A, but the equilibrium concentrations of A and B were found to be equal. The equilibrium constant (*K*) for the aforesaid chemical reaction is:

(1) 4 (2) 16

(3) $\frac{1}{4}$ (4) 1

4. Given

Gas	H_2	CH_4	CO_2	SO_2
Critical Temperature/K	33	190	304	630

On the basis of data given above, predict which of the following gases shows least adsorption on a definite amount of charcoal?

(1) SO_2 (2) CH_4

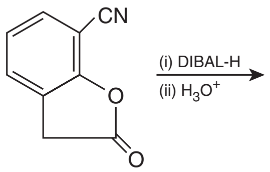
(3) CO_2 (4) H_2

5. $Mn_2(CO)_{10}$ is an organometallic compound due to the presence of:

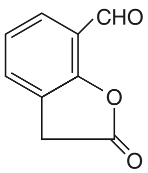
(1) Mn – C bond (2) Mn – Mn bond

(3) Mn – O bond (4) C – O bond

6. The major product of the following reaction is:



(1)



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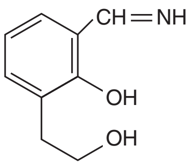

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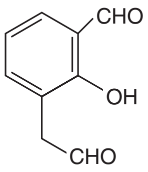

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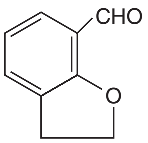


7. A metal on combustion in excess air forms X. X upon hydrolysis with water yields H_2O_2 and O_2 along with another product. The metal is:

(1) Na (2) Rb

(3) Mg (4) Li

8. The molecule that has minimum/no role in the formation of photochemical smog, is:

(1) N_2 (2) $CH_2 = O$

(3) O_3 (4) NO

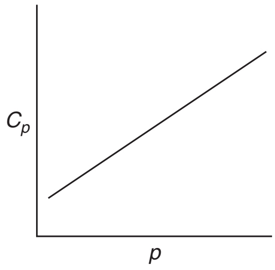
9. The pair of metal ions that can give a spin-only magnetic moment of 3.9 BM for the complex $[M(H_2O)_6]Cl_2$, is:

(1) V^{2+} and Co^{2+} (2) V^{2+} and Fe^{2+}

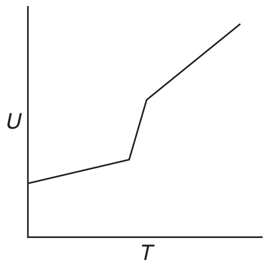
(3) Co^{2+} and Fe^{2+} (4) Cr^{2+} and Mn^{2+}

10. For a diatomic ideal gas in a dosed system, which of the following plots does not correctly describe the relation between various thermodynamic quantities?

(1)



(2)



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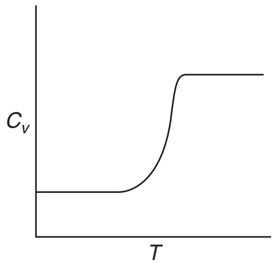

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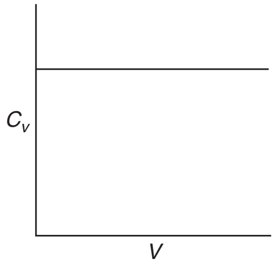


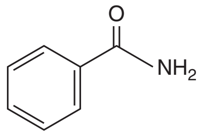
11. Among the following compounds most basic amino acid is

(1) asparagine. (2) lysine.

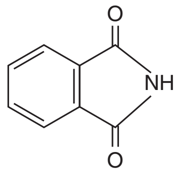
(3) serine. (4) histidine.

12. The increasing order of reactivity of the following compounds towards reaction with alkyl halides directly is:

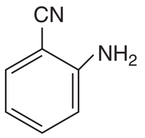
(A)



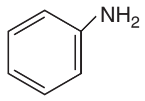
(B)



(C)



(D)



(D)

(1) (B) < (A) < (C) < (D)

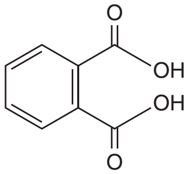
(2) (A) < (B) < (C) < (D)

(3) (B) < (A) < (D) < (C)

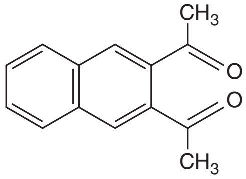
(4) (A) < (C) < (D) < (B)

13. Among the following four aromatic compounds, which one will have the lowest melting point?

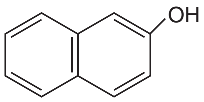
(1)



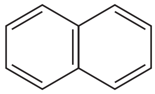
(2)



(3)



(4)



14. 50 mL of 0.5 M oxalic acid is needed to neutralize 25 mL of sodium hydroxide solution. The amount of NaOH in 50 mL of the given sodium hydroxide solution is:

(1) 40 g (2) 10 g

(3) 20 g (4) 80 g

15. The volume of gas A is twice than that of gas B. The compressibility factor of gas A is thrice than that of gas B at same temperature. The pressures of the gases for equal number of moles are:

(1) $3p_A = 2p_B$ (2) $2p_A = 3p_B$

(3) $p_A = 3p_B$ (4) $p_A = 2p_B$

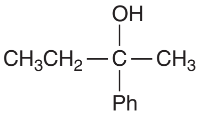
16. The hardness of a water sample (in terms of equivalents of $CaCO_3$) containing 10^{-3}M $CaSO_4$ is:

(Molar mass of $CaSO_4$ = 136 g mol^{-1})

(1) 10 ppm (2) 50 ppm

(3) 90 ppm (4) 100 ppm

17.



$CH_3CH_2-\underset{Ph}{\overset{OH}{C}}-CH_3$ cannot be prepared

(1) $CH_3CH_2COCH_3 + PhMgX$

(2) $PhCOCH_2CH_3 + CH_3MgX$

(3) $PhCOCH_3 + CH_3CH_2MgX$

(4) $HCHO + PhCH(CH_3)CH_2MgX$

18. Freezing point of a 4% aqueous solution of X is equal to freezing point of 12% aqueous motion of Y. If molecular weight of X is A then molecular weight of Y is:

(1) 3A (2) 2A
(3) A (4) 4A

19. The metal d-orbitals that are directly facing the ligands in $K_3[Co(CN)_6]$ are:

(1) d_{xy} and $d_{x^2-y^2}$ (2) $d_{x^2-y^2}$ and d_{z^2}
(3) d_{xz}, d_{yz} and d_{z^2} (4) d_{xy}, d_{xz} and d_{yz}

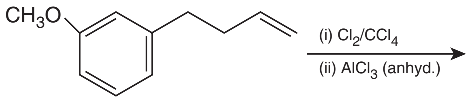
20. Decomposition of X exhibits a rate constant of 0.05 μg/year. How many years are required for the decomposition of 5 μg of X into 2.5 μg?

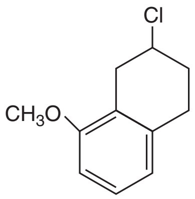
(1) 50 (2) 25
(3) 20 (4) 40

21. The standard electrode potential $E°$ and its temperature coefficient $\left(\frac{dE°}{dT}\right)$ for a cell are 2 V and -5×10^{-4} VK^{-1} at 300 K respectively. The cell reaction is $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$. The standard reaction enthalpy ($\Delta_r H°$) at 300 K in kJ mol^{-1} is, [Use $R = 8$ JK^{-1} mol^{-1} and F = 96,000 C mol^{-1}]

(1) −412.8 (2) −384.0
(3) 192.0 (4) 206.4

22. The major product of the following reaction is:



(1)


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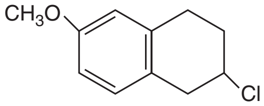
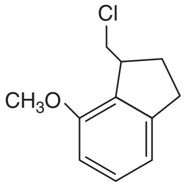


(3)


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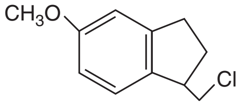


23. The element with Z = 120 (not yet discovered) will be an/a:

(1) inner-transition metal
(2) alkaline earth metal
(3) alkali metal
(4) transition metal

24. In the following reaction

$$\text{Aldehyde} + \text{Alcohol} \xrightarrow{\text{HCl}} \text{Acetal}$$

Aldehyde	Alcohol
HCHO	^tBuOH
CH_3CHO	MeOH

The best combination is:

(1) CH_3CHO and ^tBuOH
(2) HCHO and MeOH
(3) CH_3CHO and MeOH
(4) HCHO and ^tBuOH

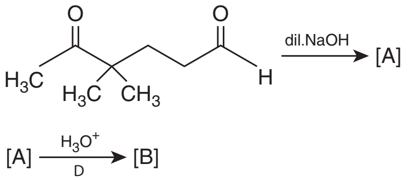
25. Two solids dissociate as follows

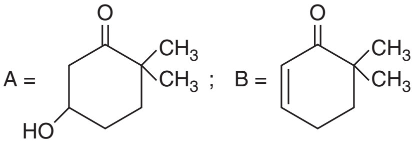
$$A(s) \rightleftharpoons B(g) + C(g);\ K_{p_1} = x \text{ atm}^2$$
$$D(s) \rightleftharpoons C(g) + E(g);\ K_{p_2} = y \text{ atm}^2$$

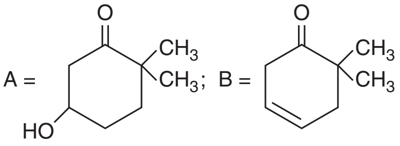
The total pressure when both the solids dissociate simultaneously is:

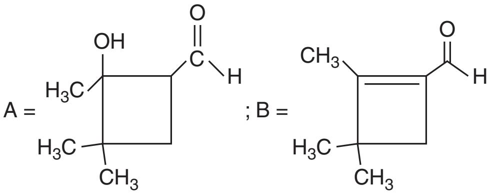
(1) $\sqrt{x+y}$ atm (2) $2(\sqrt{x+y})$ atm
(3) $(x+y)$ atm (4) $x^2 + y^2$ atm

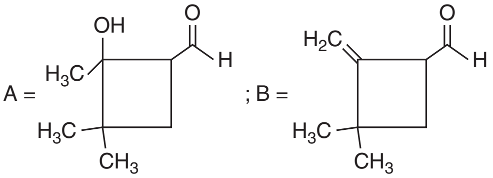
26. In the following reactions, products A and B are:



(1)


(2)


(3)


(4)


27. What is the work function of the metal if the light of wavelength 4000 Å generates photoelectrons of velocity 6×10^5 ms^{-1} from it?

(Mass of electron = 9×10^{-31} kg

Velocity of light = 3×10^8 ms^{-1}

Planck's constant = 6.626×10^{-34} Js

Charge of electron = 1.6×10^{-19} JeV^{-1})

(1) 0.9 eV (2) 3.1 eV

(3) 2.1 eV (4) 4.0 eV

28. Iodine reacts with concentrated HNO_3 to yield Y along with other products. The oxidation state of iodine in Y, is:

(1) 5 (2) 7

(3) 3 (4) 1

29. Poly-β-hydroxybutyrate-co-β-hydroxyvalerate(PHBV) is a copolymer of _____________.

(1) 3-hydroxybutanoic acid and 4-hydroxypentanoic acid

(2) 2-hydroxybutanoic acid and 3-hydroxypentanoic acid

(3) 3-hydroxybutanoic acid and 2-hydroxypentanoic acid

(4) 3-hydroxybutanoic acid and 3-hydroxypentanoic acid

30. Water samples with BOD values of 4 ppm and 18 ppm, respectively, are:

(1) Clean and clean

(2) Highly polluted and clean

(3) Clean and highly polluted

(4) Highly polluted and highly polluted

JEE Main 2019 (January 12, Shift 2)

CHEMISTRY

1. 8 g of NaOH is dissolved in 18 g of H_2O. Mole fraction of NaOH in solution and molality (in mol kg^{-1}) of the solution respectively are:

(1) 0.2, 22.20	(2) 0.2, 11.11
(3) 0.167, 11.11	(4) 0.167, 22.20

2. The magnetic moment of an octahedral homoleptic Mn(II) complex is 5.9 BM. The suitable ligand for this complex is:

(1) ethylenediamine	(2) CN^-
(3) NCS^-	(4) CO

3. The element that does NOT show catenation is:

(1) Ge	(2) Si
(3) Sn	(4) Pb

4. Among the following, the false statement is:

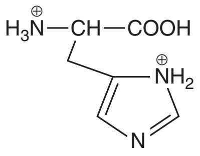
(1) It is possible to cause artificial rain by throwing electrified sand carrying charge opposite to the one on clouds from an aeroplane.

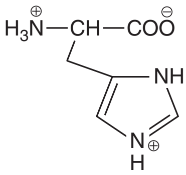
(2) Tyndall effect can be used to distinguish between a colloidal solution and a true solution.

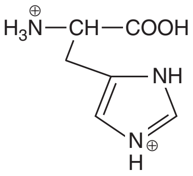
(3) Lyophilic sol can be coagulated by adding an electrolyte.

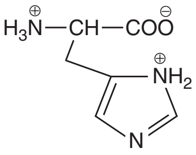
(4) Latex is a colloidal solution of rubber particles which are positively charged

5. The correct structure of histidine in a strongly acidic solution (pH = 2) is:

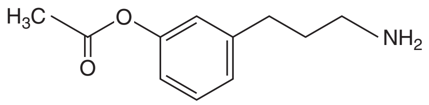
(1)


(2)


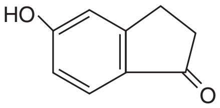
(3)


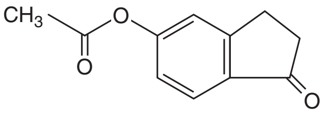
(4)


6. The major product of the following reaction is:



$$\xrightarrow[\text{(ii) } CrO_3/H^+ \quad \text{(iii) } H_2SO_4(\text{conc.}), \Delta]{\text{(i) } NaNO_2/H^+}$$

(1)


(2)


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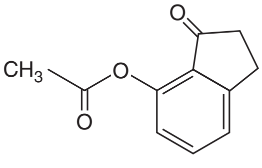
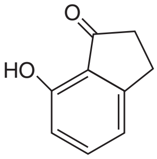


(4)


7. Λ_m° for NaCl, HCl and NaA are 126.4, 425.9 and 100.5 S cm^2mol^{-1}, respectively. If the conductivity of 0.001 M HA is 5×10^{-5} S cm^{-1}, degree of dissociation of HA is:

(1) 0.50	(2) 0.25
(3) 0.125	(4) 0.75

8. Molecules of benzoic acid (C_6H_5COOH) dimerise in benzene. '*w*' g of the acid dissolved in 30 g of benzene shows a depression in freezing point equal to 2 K. If the percentage association of the acid to form dimer in the solution is 80, then w is:

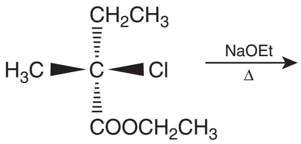
(Given that $K_f = 5$ K kg mol^{-1}, Molar mass of benzoic acid = 122 g mol^{-1})

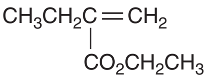
(1) 2.4 g
(2) 1.0 g
(3) 1.5 g
(4) 1.8 g

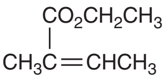
9. Chlorine on reaction with hot and concentrated sodium hydroxide gives:

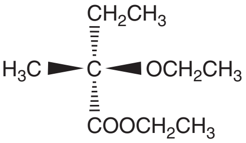
(1) Cl^- and ClO_3^-
(2) Cl^- and ClO^-
(3) ClO_3^- and ClO_2^-
(4) Cl^- and ClO_2^-

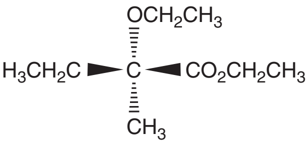
10. The major product of the following reaction is:



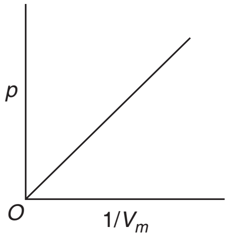
(1)

$CH_3CH_2\underset{\underset{CO_2CH_2CH_3}{|}}{C}=CH_2$

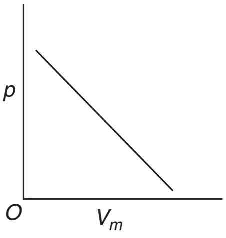
(2)

$CH_3\overset{\overset{CO_2CH_2CH_3}{|}}{C}=CHCH_3$

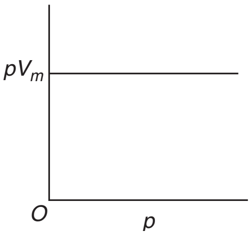
(3)


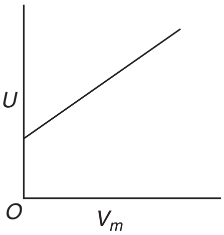
(4)


11. The combination of plots which does not represent isothermal expansion of an ideal gas is:

(A)


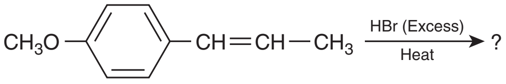
(B)


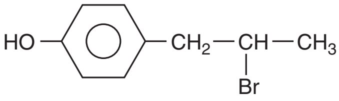
(C)


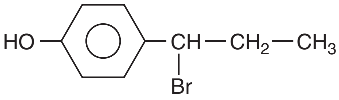
(D)


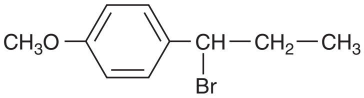
(1) (B) and (D)
(2) (A) and (C)
(3) (B) and (C)
(4) (A) and (D)

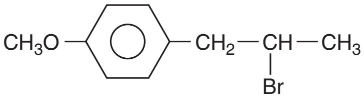
12. The major product in the following conversion is:



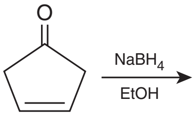
(1)


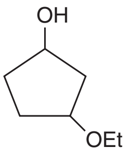
(2)


(3)


(4)


13. The major product of the following reaction is:



(1)


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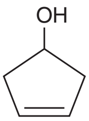
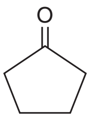
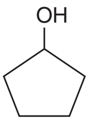


(3)


(4)


14. The correct order of atomic radii is:

(1) N > Ce > Eu > Ho
(2) Ho > N > Eu > Ce
(3) Ce > Eu > Ho > N
(4) Eu > Ce > Ho > N

15. The element that shows greater ability to form $p\pi$ - $p\pi$ multiple bonds, is:

(1) Sn
(2) C
(3) Ge
(4) Si

16. The two monomers for the synthesis of nylon 6, 6 are:

(1) $HOOC(CH_2)_4COOH, H_2N(CH_2)_6NH_2$

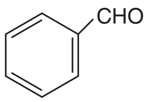
(2) $HOOC(CH_2)_6COOH, H_2N(CH_2)_6NH_2$

(3) $HOOC(CH_2)_4COOH, H_2N(CH_2)_4NH_2$

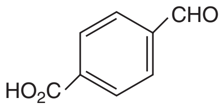
(4) $HOOC(CH_2)_6COOH, H_2N(CH_2)_4NH_2$

17. The aldehydes which will not form Grignard product with one equivalent Grignard reagents are:

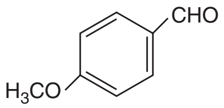
(A)



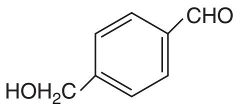
(B)



(C)



(D)



(1) (B), (D) (2) (B), (C)

(3) (B), (C), (D) (4) (C), (D)

18. Given:

(i) C (graphite) + $O_2(g) \rightarrow CO_2(g); \Delta_r H^\circ = x$ kJ mol^{-1}

(ii) C (graphite) $+\frac{1}{2}O_2(g) \rightarrow CO_2(g); \Delta_r H^\circ = y$ kJ mol^{-1}

(iii) $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g); \Delta_r H^\circ = z$ kJ mol^{-1}

Based on the above thermochemical equations, find out which one of the following algebraic relationships is correct?

(1) $x = y + z$ (2) $z = x + y$

(3) $y = 2z - x$ (4) $x = y - z$

19. The volume strength of 1 M H_2O_2 is: (Molar mass of H_2O_2 = 34 g mol^{-1})

(1) 5.6 (2) 16.8

(3) 11.35 (4) 22.4

20. The correct statement(s) among I to III with respect to potassium ions that are abundant within the cell fluids is/are:

(A) They activate many enzymes.

(B) They participate in the oxidation of glucose to produce ATP.

(C) Along with sodium ions, they are responsible for the transmission of nerve signals.

(1) A and B only

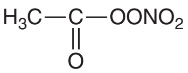
(2) A and C only

(3) A, B and C

(4) C only

21. The compound that is NOT a common component of photochemical smog is:

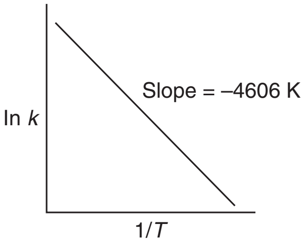
(1) O_3 (2)



$H_3C-\underset{\underset{O}{\|}}{C}-OONO_2$

(3) $CH_2{=}CHCHO$ (4) CF_2Cl_2

22. For a reaction, consider the plot of ln k versus $1/T$ given in the figure. If the rate constant of this reaction at 400 K is 10^{-5} s^{-1}, then the rate constant at 500 K is:



(1) 10^{-6} s^{-1} (2) 2×10^{-4} s^{-1}

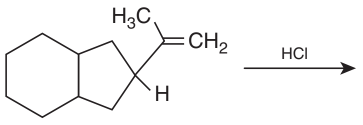
(3) 10^{-4} s^{-1} (4) 4×10^{-4} s^{-1}

23. An open vessel at 27°C is heated until two fifth of the air (assumed as an ideal gas) in it has escaped from the vessel. Assuming that the volume of the vessel remains constant, the temperature at which the vessel has been heated is:

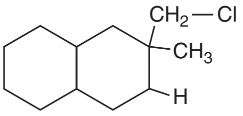
(1) 500 °C (2) 500 K

(3) 750 °C (4) 750 K

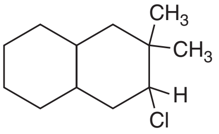
24. The major product of the following reaction is:



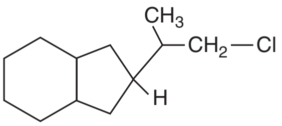
(1)

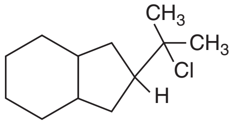


(2)

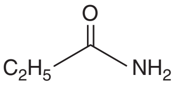


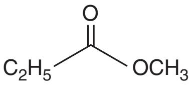
(3)

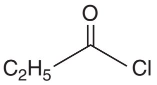


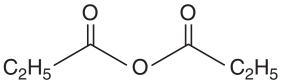
(4) 

25. The increasing order of the reactivity of the following with $LiAlH_4$ is:

(A) 

(B) 

(C) 

(D) 

(1) (B) < (A) < (C) < (D)

(2) (B) < (A) < (D) < (C)

(3) (A) < (B) < (D) < (C)

(4) (A) < (B) < (C) < (D)

26. The pair that does NOT require calcination is:

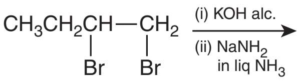
(1) ZnO and MgO

(2) ZnO and $Fe_2O_3 \cdot xH_2O$

(3) $ZnCO_3$ and CaO

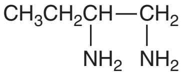
(4) Fe_2O_3 and $CaCO_3 \cdot MgCO_3$

27. The major product of the following reaction is:



$$\underset{Br}{CH_3CH_2CH}-\underset{Br}{CH_2} \xrightarrow[\text{(ii) NaNH}_2\text{ in liq NH}_3]{\text{(i) KOH alc.}}$$

(1) $CH_3CH=C=CH_2$

(2) 

$\underset{NH_2}{CH_3CH_2CH}-\underset{NH_2}{CH_2}$

(3) $CH_3CH=CHCH_2NH_2$

(4) $CH_3CH_2C \equiv CH$

28. If K_{sp} of Ag_2CO_3 is 8×10^{-12}, the molar solubility of Ag_2CO_3 in 0.1 M $AgNO_3$ is:

(1) 8×10^{-12} M (2) 8×10^{-11} M

(3) 8×10^{-10} M (4) 8×10^{-13} M

29. The upper stratosphere consisting of the ozone layer protects us from the Sun's radiation that falls in the wavelength region of:

(1) 200 – 315 nm (2) 400 – 550 nm

(3) 0.8 – 1.5 nm (4) 600 – 750 nm

30. If the de Broglie wavelength of the electron in n^{th} Bohr orbit in a hydrogenic atom is equal to $1.5\ \pi a_0$ (a_0 is Bohr radius), then the value of n/Z is:

(1) 0.40 (2) 1.50

(3) 1.0 (4) 0.75

*CHEMISTRY - JEE Main 2019 (January)– Answer Key

JANUARY 9, SHIFT 1

1. (1) **2.** (4) **3.** (3) **4.** (1) **5.** (4) **6.** (3) **7.** (4) **8.** (1) **9.** (3) **10.** (2)
11. (3) **12.** (2) **13.** (3) **14.** (1) **15.** (1) **16.** (4) **17.** (4) **18.** (2) **19.** (3) **20.** (3)
21. (1) **22.** (4) **23.** (3) **24.** (3) **25.** (1) **26.** (1) **27.** (3) **28.** (2) **29.** (2) **30.** (4)

JANUARY 9, SHIFT 2

1. (4) **2.** (3) **3.** (3) **4.** (3) **5.** (3) **6.** (4) **7.** (3) **8.** (2) **9.** (2) **10.** (2)
11. (4) **12.** (1) **13.** (3) **14.** (1) **15.** (2) **16.** (3) **17.** (2) **18.** (4) **19.** (3) **20.** (1)
21. (3) **22.** (1) **23.** (3) **24.** (1) **25.** (4) **26.** (2) **27.** (4) **28.** (4) **29.** (3) **30.** (1)

JANUARY 10, SHIFT 1

1. (4) **2.** (3) **3.** (2) **4.** (1) **5.** (1) **6.** (1) **7.** (1) **8.** (2) **9. (N*)** **10.** (3)
11. (1) **12.** (1) **13.** (2) **14.** (3) **15.** (2) **16.** (3) **17.** (2) **18.** (4) **19.** (2) **20.** (1)
21. (2) **22.** (2) **23.** (4) **24.** (1) **25.** (2) **26.** (4) **27.** (3) **28.** (4) **29.** (3) **30.** (4)

JANUARY 10, SHIFT 2

1. (3) **2.** (1) **3.** (1) **4.** (3) **5.** (1) **6.** (4) **7.** (3) **8.** (4) **9.** (3) **10.** (1)
11. (1) **12.** (4) **13.** (3) **14.** (4) **15.** (4) **16.** (4) **17.** (4) **18.** (2) **19.** (3) **20.** (4)
21. (2) **22.** (2) **23.** (4) **24.** (2) **25** (1) **26.** (1) **27.** (1) **28.** (4) **29.** (2) **30.** (4)

JANUARY 11, SHIFT 1

1. (4) **2.** (4) **3.** (3) **4.** (4) **5.** (2) **6.** (4) **7.** (1) **8.** (1) **9.** (2) **10.** (1)
11. (2) **12.** (2) **13.** (1) **14.** (3) **15.** (1) **16.** (2) **17.** (3) **18.** (1) **19.** (4) **20.** (2)
21. (3) **22.** (1) **23.** (2) **24.** (2) **25.** (3) **26.** (1) **27.** (2) **28.** (4) **29.** (2) **30.** (1)

JANUARY 11, SHIFT 2

1. (3)	**2.** (1)	**3.** (4)	**4.** (3)	**5.** (1)	**6.** (4)	**7.** (1)	**8.** (3)	**9.** (2)	**10.** (2)
11. (4)	**12.** (4)	**13.** (2)	**14.** (2)	**15.** (4)	**16.** (3)	**17.** (2)	**18.** (3)	**19.** (2)	**20.** (4)
21. (2)	**22.** (1)	**23.** (3)	**24.** (4)	**25** (1)	**26.** (4)	**27.** (3)	**28.** (1)	**29.** (1)	**30.** (2)

JANUARY 12, SHIFT 1

1. (2)	**2.** (4)	**3.** (1)	**4.** (4)	**5.** (1)	**6.** (3)	**7.** (2)	**8.** (1)	**9.** (1)	**10.** (1)
11. (2)	**12.** (1)	**13.** (4)	**14. (N*)**	**15.** (2)	**16.** (4)	**17.** (4)	**18.** (1)	**19.** (2)	**20.** (1)
21. (1)	**22.** (4)	**23.** (2)	**24.** (2)	**25** (2)	**26.** (1)	**27.** (3)	**28.** (1)	**29.** (4)	**30.** (3)

JANUARY 12, SHIFT 2

1. (3)	**2.** (3)	**3.** (4)	**4.** (4)	**5.** (3)	**6.** (1)	**7.** (3)	**8.** (1)	**9.** (1)	**10.** (2)
11. (1)	**12.** (2)	**13.** (2)	**14.** (4)	**15.** (2)	**16.** (1)	**17.** (1)	**18.** (1)	**19.** (3)	**20.** (3)
21. (4)	**22.** (3)	**23.** (2)	**24.** (4)	**25** (3)	**26.** (1)	**27.** (4)	**28.** (3)	**29.** (1)	**30.** (4)

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Note:

- **(N*) indicates question dropped. Candidate awarded full marks.**

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With over 10 years of experience in the education industry, Vipul Mehta, an IIT Bombay alumnus, has excelled in many roles in the past decade, from being a teacher, a mentor, to an administrator. He has taught over 20,000 students for Indian competitive examinations like IIT-JEE and International Olympiads and has produced numerous All India Toppers and International Chemistry Olympiad medalists.

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